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Solid State

OVERVIEW

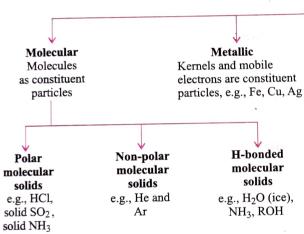
- 1. Solid: It is a form of matter which possesses rigidity and hence a definite shape and volume.

 Classification of solids (Refer to Table 1.1)
- 2.

b. Amorphous

Note: All elements and compounds (including alloys) are crystalline whereas rubber, glass, plastics, etc., are amorphous.

3. Classification of crystalline solids (on the basis of intermolecular forces in them) (Refer to Section 1.4)



a. Crystalline

Covalent

Non-metal atoms linked to adjacent atoms by covalent bond are constituent particles. They form giant molecule, e.g., diamond, SiC, SiO₂, AlN, graphite

Ionic

Positive and negative ions are constituent particles, e.g., NaCl, MgO, ZnS, CaF₂

- 4. Types of symmetry in crystals
 - **a.** Law of symmetry: It states that all crystals of a substance possess the same element of symmetry. Three important elements of symmetry are:
 - i. Plane of symmetry
- ii. Axis of symmetry
- iii. Centre of symmetry.
- **b.** The total number of elements of a symmetry in a cubic crystal = 23
 - i. Plane of symmetry = 3 (rectangular plane of symmetry)
 + 6 (diagonal plane of symmetry)
 - = 9
 - ii. Axis of symmetry = 3 (four-fold or a tetrad axis of symmetry)
 - + 4 (three-fold or triad axis of symmetry)
 - + 6 (two-fold or diad axis of symmetry) = 13

- iii. Centre of symmetry or inversion of symmetry = 1
 ∴ Total number of elements of symmetry in a cubic crystals = 9 + 13 +1 = 23
- c. Axis of six-fold or a hexad axis of symmetry: This type of symmetry is possible in hexagonal crystals and not in cubic crystals.
- 5. Crystal lattice and unit cells
 - **a.** A crystal lattice is a 3-D arrangement of constituent particles in a crystal.

A unit cell is the smallest portion of a crystal lattice which when repeated in different directions gives the entire lattice.

Thus, for a 3-D lattice, a unit cell is described by three edges (a, b, and c) and angles between then $(\alpha, \beta, \text{ and } \gamma)$.

b. Seven crystal systems and 14 Bravais lattice: Just as there are five possible 2-D lattices, there are seven crystal systems which constitute 14 possible 3-D lattices and are called Bravais lattices.

6. a. Close-packed structures in three dimensions: Hexagonal close packing (hcp) is ABA-ABA... arrangement of layers in which tetrahedral voids (TVs) of second layer are covered by the spheres of third layer. This arrangement of atoms is found in metals such Mg and Zn.

Cubic close packing (ccp) is ABC-ABC... arrangement of layers in which the third layer is placed above the second layer in a manner such that its spheres cover the octahedral voids (OVs). This is also called facecentred cubic (fcc) structure. Metals such as Cu and Ag crystallize in this structure.

- b. fcc or ccp and hcp are close packed arrangements in which the coordination number is 12, 74% space is occupied, and 26% is empty while bcc is not a close packed arrangement and has a coordination number of 8, 68% space occupied, and 32% is empty.
- 7. a. Number of atoms present in a close packed structure = Number of octahedral voids = 4 per unit cell
 - **b.** Number of $TVs = 2 \times OVs = 2 \times Number of atoms in$ a close packed structure = 8/unit cell
 - c. Number of TVs = $2 \times$ Number of occupied voids
 - d. Number of atoms (or ions) present in a close packed structure (fcc or ccp) = 4/unit cell

Number of TVs = 8/unit cell =
$$\frac{8}{4}$$
 = 2/atom

Number of OVs = 4/unit cell = $\frac{4}{4}$ = 1/atom.

8. Radius of TV = 0.225r

Radius of OV = 0.414r

where r is the radius of ions (mostly cations) in the packing.

- 9. Location of TVs and OVs in a close packed structure (Refer to Section 1.14.4)
- 10. Radius ratio rule

Radius ratio =
$$\frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{r_{\oplus}}{r_{\odot}} \text{ or } \frac{r_{\text{c}}}{r_{\text{a}}} \text{ or } \frac{r}{R}$$

11. Structures of ionic crystals

Ionic compounds have any one of the following three types of structures:

- a. AB type: Rock salt (NaCl) type, CsCl-type structure, zinc blende (Zns) or sphalerite-type structure.
- **b.** AB₂ type: Fluorite type, e.g., CaF₂, BaF₂, etc.
- c. A₂B type: Antifluorite type, e.g., Na₂O, Li₂O, etc.
- d. Ligancy as a function of radius ratio in 1:1 or ABtype structure (Refer to Table 1.11)
- 12. Hexagonal close packed structure (hcp)
 - **a.** Z_{eff} in hcp = 6/unit cell = Number of OVs Number of TVs = $6 \times 2 = 12$ /unit cells
 - **b.** Base area of hexagon = $6\sqrt{3}r^2$

- **c.** Height of hexagon $(c) = 4r \times \sqrt{\frac{2}{2}}$ $=2a\times\sqrt{\frac{2}{3}}$
- **d.** Volume of unit cell of hexagon = $24\sqrt{2}r^3$
- e. Packing fraction = $\frac{6 \times \text{Volume of atom}}{\text{Volume of unit cell}}$ $=\frac{6\times\frac{4}{3}\pi r^3}{24\sqrt{2}r^3}=\frac{\pi}{3\sqrt{2}}=0.74$
- f. $\frac{c}{a}$ ratio of ideally close packed hcp crystal:

$$\frac{c}{a} = \frac{4r}{2r}\sqrt{\frac{2}{3}} = 2\sqrt{\frac{2}{3}} = 1.633$$

13. Effect of temperature and pressure on the crysta structure

On the application of high pressure, NaCl-type structure (6: 6 coordination) transform to CsCl-type structure (8: 8 coordination), while on heating reverse occurs. NaCl-type structure Pressure CsCl-type structure (8:8 coordination) (6:6 coordination)

- 14. Structure of diamond cubic (dc) (Refer to Section 1.17)
- 15. Normal spinel structures (AB,Oa) (Refer to Section 1.18.1)
- 16. Inverse spinel structure (AB, O_4) type (Refer to Section 1.18.2)
- 17. Corundum structure (A₂O₃ type) (Refer to Section 1.19)
- 18. Structure of red brown α -Fe₂O₃ [Refer to Section 1.19.1(b)]
- 19. Structure of Fe₃O₄ (FeO·Fe₂O₃ or FeO·Fe₂O₃) It has inverse spinel structure. [Refer to Section 1.19.1(d)]
- 20. Perovskite structure (BaTiO₃) (Refer to Section 1.20)
- 21. Rutile structure (TiO₂) (Refer to Section 1.21)
- 22. a. Void volume in ionic compound Void volume per unit volume of unit cell

= 1 - Packing fraction

- b. Refer to Table 1.12 for summary of the main character istics and examples of some simple ionic solids.
- 23. a. Law of rational indices (Hauy's law): Refer to Section 1.24.

- **b.** Weiss indices: The coefficients of unit intercepts (a, b, c, i.e., l, m, n) are known as Weiss indices of a plane. For example, for a crystal plane which cuts through the crystal axis at (2a, 3b, c), the Weiss indices = 2, 3, 1.
- c. Miller indices: Reciprocal of the Weiss coefficients and multiplying through by the smallest number that will express all the reciprocals as integers.

For example: Weiss indices $= 2 \quad 3$

Reciprocal =
$$\frac{1}{2}$$
 $\frac{1}{3}$ $\frac{1}{1}$

Simplifying
$$= 3 2 6$$

Miller indices are (3 2 6).

d. d-spacing: The distance between two parallel planes in a cubic crystal is given by:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a = edge of the cube, and h, k, and l are Miller indices of the parallel plane.

e. d-spacing for sc, fcc, and bcc

For sc:
$$d_{100}$$
: d_{110} : $d_{111} = a$: $\frac{a}{\sqrt{2}}$: $\frac{a}{\sqrt{3}}$

For fee:
$$d_{200}$$
: d_{220} : $d_{111} = \frac{a}{2}$: $\frac{a}{2\sqrt{2}}$: $\frac{a}{\sqrt{3}}$

For bcc:
$$d_{200}$$
 : d_{110} : $d_{222} = \frac{a}{2}$: $\frac{a}{\sqrt{2}}$: $\frac{a}{2\sqrt{3}}$

- 24. a. Polymorphism: The occurrence of different crystal forms of the same substance is called polymorphism. For example, ZnS (zinc blende) and ZnS (wurtzite).
 - **b.** Allotropy: Polymorphism occurring in elements is called allotropy. Allotropy can be of three types:
 - i. Enantiotropy: One form is interconvertible to another at a fixed transition temperature under specified pressure, e.g., at 96.6°C, rhombic S is converted to monoclinic S and vice versa.
 - ii. Monotropy: One form is unstable at all temperatures and is converted to stable form, e.g.,

$$O_2 \longrightarrow O_3$$
, red $P_4 \longrightarrow$ yellow P_4 .

- iii. Dynamic allotropy: Both forms exist side by side in equilibrium at all temperatures, e.g., λ and μ sulphur.
- c. Isopolymorphism: If each of the two different forms of a polymorphic substance is isomorphous with a form of another polymorphic substance, then it is called isopolymorphism.
- d. Law of isomorphism: According to Mitscherlich, isomorphous substances have similar chemical constitution, i.e., they have the same number of atoms similarly arranged and therefore have same formula. For example, K₂SO₄ and K₂CrO₄; ZnSO₄·7H₂O and MgSO₄·7H₂O are isomorphous.

25. Imperfections in solids

- **a.** Irregularities in the arrangement of constituent particles are called *defects*.
- **b.** Impurity defect: This defect is due to the presence of foreign atoms at lattice sites (in place of host atoms)

- or at vacant interstitial sites. For each Ba²⁺ or Sr²⁺ ion introduced into NaCl crystal one hole is created (one vacancy) which makes NaCl as a semi-conductor.
- c. The number of Schottky defects present in an ionic crystal containing N ions at temperature T is given by: $n = Ne^{-E/2KT}$,

where E is the energy required to create these n Schottky defects and K is the Boltzmann constant and is equal to

$$= \frac{R}{N_{\Lambda}} = 1.38 \times 10^{23} \text{ J K}^{-1}.$$

d. The number n of Frenkel defects in an ionic crystal containing N ions and N_i , the number of interstitial sites at a temperature T, is given by:

$$n = \left(\frac{N}{N_{\rm i}}\right)^{\frac{1}{2}} e^{-E/2KT}$$

where E is the energy required to create n Frenkel defects.

For NaCl at 1000 K, the energies of formation of these defects are 2 eV and 3 eV, respectively (1 eV = 1.602×10^{-19} J).

e. Fraction of the surface of a crystal vacancy is given by:

$$\frac{n}{N} = e^{-E/RT}$$

26. a. Conduction of electricity in metals and semiconductors: Metallic conductors conduct electricity due to the movement of electrons while electrolytes conduct electricity due to the movement of ions.

The conductivity of metals depends upon the number of valence electrons available per atom. These atomic orbitals of metal atoms form molecular orbital which are so close in energy to each other as to form a band

In metals, there is no gap between valence band and conduction band. Hence, electrons can flow easily under an applied electric field and the metal shows conductivity.

In insulators, the gap between valence band and conduction band is large; electrons cannot jump to over it and such a substance has very low conductivity.

In *semiconductors*, the gap between valence and conduction band is small, hence some electrons may jump to conduction band and show some conductivity. Si and Ge show this type of behaviour and are called *intrinsic semiconductors*. The conductivity of a semiconductor increases with rise in temperature.

- b. Doping: The conductivity of an intrinsic semiconductor increases by adding a suitable impurity. This process is called doping, and it can be done by adding an impurity which is electron rich or electron deficient as compared to Si or Ge. Such impurities introduce electronic defects.
- c. Electron-rich impurities (*n*-type semiconductor): When Si (Group 14) is doped with phosphorous (Group 15), unshared electrons make Si *n*-type (negatively charged electron) semiconductor.

- d. Electron-deficient impurities (p-type semiconductor): When Si (Group 14) is doped with aluminium (Group 13), holes are created and Si becomes p-type (positively charged holes) semiconductor.
- **Diode:** It is a combination of n-type and p-type semiconductors and is used as a rectifier.
- Transistors: They are made by sandwiching a layer of one type of semiconductor between two layers of other type of semiconductor. npn and pnp type of transistors are used to detect or amplify radio or audio signals.
- Group 13-15 compounds are InSb, AlP, and GaAs. In, Al, Ga (Group 13) and Sb, P, As (Group 15) elements.
- h. Group 12-16 compounds are ZnS, CdS, CdSe, and HgTe. Zn, Cd, Hg (Group 12) and S, Se, Te (Group 16) elements.
- 27. Magnetic properties: Substances are classified into five categories on the basis of their magnetic properties:
 - a. Diamagnetism: Such substances are weakly repelled by a magnetic field. It is shown by those substances which have all paired electrons, e.g., H₂O, NaCl, and C₆H₆. They are weakly magnetized in magnetic field in opposite direction.
 - b. Paramagnetism: Such substances are weakly attracted by a magnetic field. It is shown by those substances which have one or more unpaired electrons. They are magnetized in magnetic field in the same direction, e.g., O₂, Cu²⁺, Fe³⁺, Cr³⁺. They lose their magnetism when magnetic field is removed.
 - c. Ferromagnetism: Such substances remain permanently magnetized even when magnetic field is removed. For example, Fe, Co, Ni, and CrO₂.
 - d. Antiferromagnetism: Such substance have zero magnetic moment because there are equal number of electrons with opposite spin. For example, MnO.

- Ferrimagnetism: Such substances have small magnetin moment because they have unequal number of electron with opposite spin. For example, Fe₃O₄, MgFe₂O₄, and $ZnFe_2O_4$.
 - These substances also lose ferrimagnetism on heating and become paramagnetic.
- Curie temperature: The temperature above which no ferromagnetism is observed is known as curie temperature.
- 28. Dielectric properties or electrical properties of polar crystals: Polar crystals are classified into five categories on the basis of their electrical properties.
 - a. Piezoelectricity: When mechanical stress is applied on a polar crystal, electricity is produced due to the displacement of ions. For example, PbZrO₃, NH₄H₂PO₄ and quartz.
 - b. Pyroelectricity: The electricity produced on heating a polar crystal is called pyroelectricity.
 - c. Ferroelectricity: Ferroelectric crystals remain permanently polarized even in the absence of electric field. For example, BaTiO₃, Rochelle Salt, KH₂PO₄.
 - d. Antiferroelectricity: Antiferroelectric crystals have net zero dipole moment because they have equal number of opposite dipoles. For example, PbZrO3.

Note: All ferroelectric crystals are piezoelectric but reverse is not true.

e. Superconductivity: When the electrical resistance of a substance becomes almost zero, it is called superconductor. For example, YBa₂Cu₃O₇ at 90 K.

Note:

- i. Hg becomes superconductor at 4 K.
- ii. Amorphous silica is used in making photovoltaic cell (to convert sunlight into electricity).

Matter can be classified into three categories depending upon its physical state, namely, solid, liquid, and gas.

1.2 GENERAL CHARACTERISTICS OF SOLID STATE

Under a given set of conditions of temperature and pressure, whether a substance will exist as a solid, liquid, or gas depends upon the net effect of two opposing factors:

- a. Intermolecular forces: These forces exist among the constituent particles (atoms, molecules, or ions) and tend to keep the molecules closer.
- **b. Thermal energy:** This energy among the constituent particles is due to temperature and tends to keep them apart by making them move faster.

At sufficiently low temperature, the thermal energy is low, but intermolecular forces are so strong that the particles come so close that they cling to one another and occupy fixed positions and are unable to move. They can still oscillate about their mean positions and the substance exists in solid state.

Some of the common characteristics of solids which distinguish them from the other two states of matter are:

- **a.** Solids have definite volume irrespective of the size or shape of the container in which they are placed.
- **b.** Solids are rigid and have definite shapes.
- **c.** Many solids have a crystalline appearance and have definite pattern of angles and planes.
- **d.** Solids are almost incompressible, having compressibility approximately 10^6 times more than gases.
- **e.** Solids have a much higher density (mass-to-volume ratio) than that of gases or liquids.
- **f.** Solids diffuse very slowly as compared to liquids or gases. Constituent particles are very closely packed in solids permitting very little space for their movement.
- g. Most solids become liquid when heated. Some undergo sublimation on heating. The temperature at which a solid changes into liquid is called *melting point* and the process is called as *melting*. Due to the varying nature of solids, their melting temperatures vary considerably.

1.3 CLASSIFICATION OF SOLIDS

On the basis of the nature of order present in the arrangement of their constituent particles, solids are classified as crystalline or amorphous.

1.3.1 CRYSTALLINE SOLIDS

All solid elements (metal and non-metals) and compounds exist in crystalline form. In a crystal, the arrangement of constituent particles is of long range order. It usually consists of a large number of small crystals each of which has the same regular pattern or arrangement of particles. This arrangement repeats itself periodically over the entire crystal.

Crystalline solids have a sharp (characteristic) melting point. They are anisotropic in nature, that is, they show different physical

properties such as refractive index, electrical resistance (or conductance), thermal expansion, etc., along different directions in the same crystal. This is due to different arrangement of particles in different directions, which results in the value of same physical property to be different along each direction, as shown in Fig. 1.1. NaCl and quartz are some examples of crystalline solids.

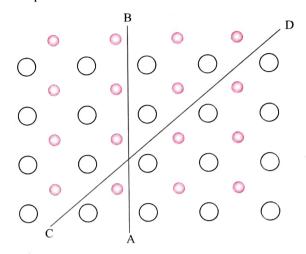


Fig. 1.1 Anisotropy in crystals due to different arrangement of particles along different directions

1.3.2 AMORPHOUS SOLIDS

In amorphous solid (Greek: a without; morphe'shape, form), the arrangement of constituent particles is of short range order and consists of particles of irregular shape. In such an arrangement, a regular and periodically repeating pattern is short distance only. Such portions are scattered and in between the arrangement is disordered. Crystalline solids are isotropic in nature because there is no long range order in them and the arrangement is irregular along all the direction. That is, they show similar physical properties (like, refractive index, electrical resistance or conductance, thermal expansion, etc.) along any direction.

The structures of quartz (crystalline) and quartz glass (amorphous), respectively, are almost identical. Yet in the case of amorphous quartz glass, there is no long range order, and its structure is similar to that of liquids. Glass, rubber, and plastics are some examples of amorphous solids.

In fact, only the crystalline solids are *true solids* whereas amorphous solids are considered to be highly supercooled liquids of very high viscosity and are called *pseudosolids*. Like liquids, amorphous solids have a tendency to flow slowly. This is supported by the fact that the glass panes fixed in the windows or doors of old buildings are found to be slightly thicker at the bottom than at the top. This is because glass flows down very slowly and makes the bottom portion slightly thick.

Moreover, due to short range order in amorphous compounds, small parts of an amorphous solid crystallizes while rest does not crystallize. This is also supported by the fact that some glass objects from ancient civilization are found to become milky in appearance because of crystallization.

The main points of distinction between crystalline and amorphous solids are summarized in Table 1.1.

lab	le 1.1 Distinction be	etween crystalline and amorphous solids	Amorphous solids
	Properties	Crystalline solids	They do not have sharp melting points.
a.	Melting point	They have sharp melting points.	The internal arrangement of particles is irregular
b.	Crystal geometry	They have sharp meeting per The internal arrangement of particles is regular, so they possess definite and regular geometry. They have long	Thus, they do not have any definite geometry. They have short range order.
		range order.	They do not have characteristic heat of fusion.
c.	Heat of fusion	They have characteristic heat of fusion. They have characteristic heat of fusion.	A morphous solids are comparatively soft and
d.	Physical state	Crystalline solids are hard and rigid, shape is not distorted by mild distorting forces.	very rigid. These can be distorted by bending compressing forces.
e.	External form	There is regularity in the external form when crystals are formed. Crystalline solids give a regular cut when cut with a sharp-edged knife.	There is no regularity in the external form who amorphous solids are formed. Amorphous solid give irregular cut.
		with a snarp-edged kine.	Amorphous solids are isotropic in nature. The
isotropic nature	Crystalline solids are anisotropic. This implies that physical properties such as refractive index, conductivity, thermal expansion, etc., are different in different directions. This is due to orderly arrangement of particles.	implies that various physical properties are san in all the directions. This is because of the rando arrangement of particles.	
e.	Examples	Crystals of NaCl, CsBr, CaF ₂ , and ZnS.	Rubber, glass, and plastic.

Note: Some substances adopt different arrangements under different conditions. Such compounds are called as polymorphs. These different structures have different properties such as melting point, density, etc. For example, diamond and graphite are two different polymorphic forms of carbon.

1.4 CLASSIFICATION OF CRYSTALLINE SOLIDS

Most of the solid substances are crystalline, for example, metallic elements such as Fe, Ag, Au, Cu, and non-metallic elements such as phosphorous (P_4) , sulphur (S_8) , and I_2 . Compounds such as NaCl, ZnS, and naphthalene form crystalline solids.

They are further classified on the basis of the nature of intermolecular forces in them into four types (a) molecular, (b) metallic, (c) covalent, and (d) ionic solids.

1.4.1 MOLECULAR SOLIDS

The constituent particles in molecular solids are molecules. They are further subdivided into the following types:

a. Polar molecular solids: They are formed by covalent bonds. The molecules are held by relatively stronger dipole-dipole interactions (Fig. 1.2). Their melting points are higher than those of non-polar molecular solids. These solids are soft and non-conductors of electricity. Some of them are gases or liquids under room temperature and pressure.

Example: HCl, solid SO_2 , and solid NH_3 .

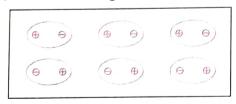


Fig. 1.2 Dipole-dipole force of attraction

b. Non-polar molecular solids: They are formed by either atoms (e.g., He and Ar) or molecules formed by nonpolar covalent bonds (e.g., H2, Cl2, and I2). The atoms or molecules are held by weak dispersion forces or London forces (Fig. 1.3). Like polar molecular solids, they are also soft and non-conductors of electricity. But their melting points are lower than those of polar molecular solids. They are usually present in liquid or gaseous state at room temperature and pressure.

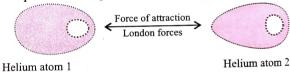


Fig. 1.3 Weak London dispersion forces

c. Hydrogen-bonded molecular solids: In such solids, the molecules contain polar covalent bonds between H and F, O, or N atoms. Hence, the intermolecular forces of attraction in these molecules are the strong hydrogen bonds, e.g., H₂O (ice), NH₃, ROH, glycol (HOCH₂—CH₂OH). etc.

They are volatile liquids or soft solids at room temperature and pressure. They are non-conductors of electricity. Their melting and boiling points are generally higher than the molecular solids of the first two types.

METALLIC SOLIDS 1.4.2

In such solids, the constituent particles are orderly arranged positively charged metal ions (called kernels) surrounded by sea of free electrons. These electrons are mobile and are evenly spreaded out throughout the crystal and flow throughout the meta crystal such as water in the sea. These are produced from meta atoms having low ionization energy and can easily lose the valence electrons to leave behind positively charged ions (kernels) Each metal atom contributes one or more electrons towards thi sea of mobile electrons. Hence, it is called electron sea model.

Metallic bonding is also explained by *electron gas model* because the electrons are free to move in all directions like the molecules of a gas. These mobile electrons are simultaneously attracted by the positive ions (*kernels*) and hence hold these positive ions together. The force that holds the metal ions together in the crystal is called metallic bond. Greater the number of mobile electrons, greater is the force of attraction, and hence stronger is the metallic bonding resulting in high melting and boiling points.

Following are the characteristics properties of metallic solids:

- a. They possess high electrical and thermal conductivity. When an electrical field is applied, the mobile electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of the metal, the thermal energy is uniformly spreaded throughout by free electrons.
- **b.** They possess lusture and colour in certain cases. This is also due to the presence of free electrons in them.
 - When visible light falls on the metal, the free electrons oscillate about their mean position and reflect light in all directions and thus are lustrous.
- c. They are highly malleable and ductile. This is because of the non-directional nature of the metallic bonding. On beating, one layer of metal slides over the other because the position of the positive ions can be altered without destroying the crystal lattice and also the uniform charge distribution provided by mobile electrons. For these reasons they can be moulded into sheets and wires.
- **d.** They have high melting points and high densities due to the close packing of the positive ions in the crystal and due to high metallic bonding.

1.4.3 COVALENT OR NETWORK SOLIDS

In covalent solids, the constituent particles are non-metal atoms linked to the adjacent atoms by covalent bonds throughout the crystal. As a result, a network of covalent bond is formed. Hence, they form *giant molecules*.

Diamond and silicon carbide (SiC) (or called carborundum) are some examples of such solids. In diamond, the C-atoms are linked

together by covalent bond to give a three-dimensional structure.

Following are the characteristic properties of covalent solids:

- **a.** They are very hard and brittle since covalent bonds are strong and directional in nature.
- **b.** They have extremely high melting points and may even decompose before melting.
- c. They are insulators and do not conduct electricity.

Exception: Graphite is soft and a conductor of electricity. Its exceptional properties are due to its typical structure. The C-atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is a conductor of electricity due to these free electrons. Graphite is a soft solid and a good lubricant because different layers in graphite can slide over the other.

1.4.4 IONIC SOLIDS

In ionic solids, the constituent particles are positive and negative ions. Such solids are formed by the three-dimensional arrangement of positive (cations) and negative (anions) ions held by strong electrostatic (coulombic) force of attraction.

The characteristics of ionic solids are as follows:

- **a.** They have high melting and boiling points due to strong electrostatic force of attraction.
- **b.** They are electric insulators in the solid state because their ions are not free to move about. However, in the molten state or when dissolved in water, the ions become free to move about and hence they conduct electricity.
- **c.** They are soluble in polar solvents but insoluble in non-polar solvents.
- **d.** They are hard due to strong electrostatic forces of attractions and the ions are closely packed.
- e. They are brittle because their stability depends upon the retention of their geometrical pattern.

The different properties of the four types of crystalline solids are summarized in Table 1.2.

Table 1.2 Different types of solids

	Type of solid	Constituent particles	Bonding/ attractive forces	Examples	Physical nature	Electrical conductivity	Melting point
1.	Molecular solids a. Non-polar b. Polar	Molecules	Dispersion or London forces dipole-dipole interactions	Ar, CCl_4 , H_2 , I_2 , CO_2 HCl , SO_2	Soft Soft	Insulator Insulator	Very low Low
	c. Hydrogen bonded		Hydrogen bonding	H ₂ O (ice)	Hard	Insulator	Low
2.	Metallic solids	Positive ions in a sea of delocalized electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high

1.8	Physical Chemistry			SiO ₂	Hard	Insulators	Very high
3.	Covalent or network solids	Atoms	Covalent bonding	(quartz), SiC, C (diamond), AIN,		Conductor (exception)	
				C _(graphite)	Soft		
4.	Ionic solids	Ions	COUNTRACTOR	NaCl, MgO, ZnS, CaF ₂	Hard but brittle	Insulators in solid state but conductors in molten state and in	High

1.5 TYPES OF SYMMETRY IN CRYSTALS

Crystals possess a regular, repetitive internal structure. The concept of symmetry describes the repetition of structural features. Crystals therefore possess symmetry, and crystallography is basically concerned with describing different types of symmetry. Broadly, two general types of symmetry exist. These consist of translational symmetry and point symmetry. Translational symmetry describes the periodic repetition of a structural feature across a length or through an area or volume. The concept of a lattice is directly related to the idea of a translational symmetry. Point symmetry, on the other hand, describes the periodic repetition of a structural feature around a point. Reflection, rotation, and inversion are all point symmetries. These are explained as below:

- a. Reflection/plane of symmetry: It is an imaginary plane which passes through the centre of crystal and divides it into two equal portions such that one part is exactly the mirror image of the other. A cubic crystal such as NaCl possesses, in all, nine planes of symmetry: three rectangular and six diagonal planes of symmetry.
 - i. Rectangular plane of symmetry: These are the planes situated midway parallel to the opposite faces. Since a cube has six faces, so it has three rectangular planes of symmetry as shown in Fig. 1.4.

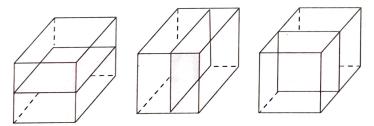
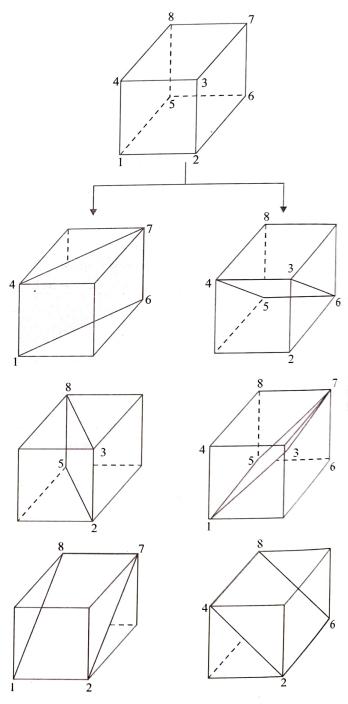


Fig. 1.4 Rectangular planes of symmetry

ii. Diagonal plane of symmetry: These are the planes touching the opposite edges. They lie on the diagonal of opposite faces. Since there are 12 edges or 6 pairs of opposite edges in a cubic crystal, as much as six diagonal planes of symmetry are possible in a cubic crystal (Fig. 1.5).



aqueous solutions

Fig. 1.5 Diagonal planes of symmetry

Thus, planes of symmetry in cubic crystal

- = 3 rectangular planes of symmetry + 6 diagonal planes of symmetry
- = 9 planes of symmetry

b. Rotational symmetry/axis of symmetry

Axis of line of symmetry: It is an imaginary line (or axis) about which the crystal may be related so that it presents the same appearance more than once in a complete rotation through 360°. In a cubic crystal, the axis of symmetry may be of three types depending upon the number of times the identical appearance occurs during the course of a complete rotation of 360°.

i. Axis of four-fold symmetry: Imagine a line passing through the centres of two opposite faces of a cube. On rotating the cube above this line as axis, the self coincidence (identical appearance) of the cube occurs four times during the course of rotation through 360°, i.e., the original appearance is repeated as a result of rotation through 90°. Such an axis is said to be an axis of four-fold symmetry or a tetrad axis. Now since there are six faces or three pairs of opposite faces in a cubic crystal, three such axes at right angle to each other are possible (Fig. 1.6).

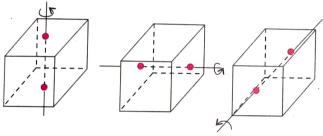


Fig. 1.6 Axis of four-fold symmetry

ii. Axis of two-fold symmetry: Imagine a line passing through the centres of the two diagonally opposite edges of a cube. On rotating the cube about this line as axis, the identical appearance of the cube occurs twice during the course of rotation through 360°, i.e., the original appearance is repeated as a result of rotation through 180°. Such an axis is said to be an axis of two-fold symmetry or a diad axis. Since there are 12 edges or six such diagonally opposite pairs of edges in a cubic crystal, six such axes are possible (Fig. 1.7).

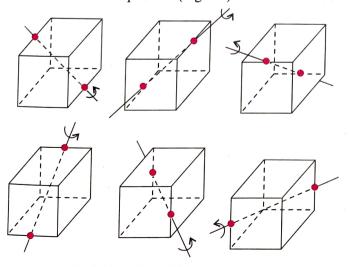


Fig. 1.7 Axis of two-fold symmetry

iii. Axis of three-fold symmetry: Imagine a line passing through the opposite corners of a cube along the body diagonal. On rotating the cube about this line as axis, the identical appearance of the cube occurs three times during the course of rotation through 360°, i.e., the original appearance is repeated as a result of rotation through 120°. Such axis is said to be an axis of three-fold symmetry or a triad axis. Now since there are eight corners or four such body diagonally opposite pairs of corners of cubic crystal, four such axes are possible (Fig. 1.8).

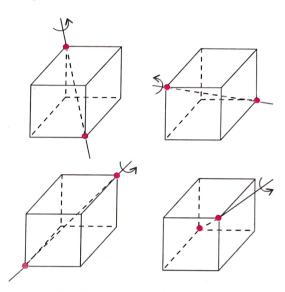


Fig. 1.8 Axis of three-fold symmetry

Thus, in a cubic crystal, there are three axes of four-fold symmetry, four axes of three-fold symmetry, and six axes of two fold symmetry. Thus, in all, a cubic crystal has 3 + 4 + 6 = 13 axes of symmetry.

c. Inversion symmetry or centre of symmetry: It is such a point in the crystal that any line drawn through it intersects the surface of the crystal at equal distances on either side. A crystal may have one or more planes or axes of symmetry but it never has more than one centre of symmetry which lies at the centre of the cube (Fig. 1.9).

The total number of elements of symmetry in a cubic crystal are 23.

Planes of symmetry = 3 + 6 = 9

Axes of symmetry = 3 + 4 + 6 = 13

Centre of symmetry = 1

 \therefore Total number of elements of symmetry = 9 + 13 + 1

= 23

Axis of six-fold symmetry: This axis of symmetry is possible in hexagonal crystals and not in cubic crystals. Imagine a line passing through the centres of two opposite hexagonal faces of a hexagonal crystal. On rotating the crystal (hexagonal) about this line as axis, the identical appearance of the hexagon occurs six times in the course of one complete rotation of 360°, i.e., the original appearance is repeated as a result of rotation through 60°. Such an axis is, therefore, known as axis of six-fold symmetry or a hexad axis.

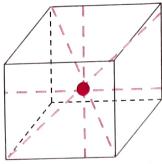


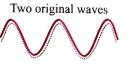
Fig. 1.9 Inversion symmetry/centre of symmetry

1.6 X-RAY STUDY OF CRYSTALS

- a. X-ray diffraction: X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and synthetic materials.
 - It was suggested by Max von Laue, in 1913, that it might be possible to diffract X-rays by means of crystals. The reason for the suggestion was that the wavelength of X-rays was of about the same order (10⁻⁸ cm) as the inter-atomic distances in a crystal. In fact, Bragg succeeded in diffracting X-rays from sodium chloride crystals. This observation has proved to be highly useful in determining structures and dimensions of crystals as well as in the study of a number of properties of X-rays themselves.
- b. Structure determination by X-ray: If we look through a piece of thin stretched cloth against bright light, we find a pattern caused by the deflection of light as it passes through the regular space threads of the fabric. The deflection of light is called diffraction and the patterns produced are called diffraction patterns. From the diffraction pattern, it is possible to deduce the arrangement of strands in the fabric. The same idea is used to determine the arrangement of atoms/ions in a crystal. Max von Laue visualized that a crystal can act as a three-dimensional grating for the diffraction of X-rays. In 1912, he obtained a diffraction pattern produced by passing X-rays through a crystal of copper sulphate. W.L. Bragg and his father W.H. Bragg determined the cubic structure of sodium chloride using X-rays. These days, the structure of extremely complex substances such as proteins and nucleic acids is determined using the technique.

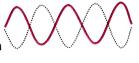
When a beam of X-rays falls on a crystal plane composed of regularly arranged atoms or ions, the X-rays are diffracted. Waves from the diffracted X-rays may interfere and destroy each other (Fig. 1.10). However, it is also possible that X-rays diffracted by the particles (atoms/ions) can also reinforce each other producing constructive interference.

(a) Waves in phase, coincide, and reinforce each other





(b) Waves out of phase, interfere, and destroy each other



No signal

Fig. 1.10 (a) Constructive and (b) destructive interference of $\chi_{-r_{a}y_{s}}$

In a crystalline solid, the constituent particles (atom_§, ions, or molecules) are arranged in a regular order. A_{h} interaction of a particular crystalline solid with X-rays $hel_{p_{\S}}$ in investigating its actual structure.

Crystals are found to act as diffraction gratings for X-rays and this indicates that the constituent particles in the crystals are arranged in planes at close distances in repeating patterns.

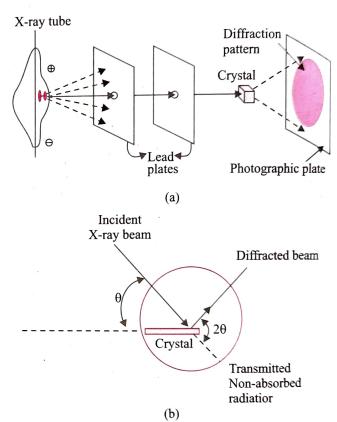


Fig. 1.11 Study of X-ray diffraction

A simple representation of the X-ray diffraction is shown in Figs. 1.11(a) and 1.11(b).

c. Bragg's equation

W.H. Bragg pointed out that the scattering of X-rays by crystals could be considered as reflection from successive planes of atoms in the crystals.

The process was based upon the principle that a crystal may be considered to be made up of a number of parallel equidistant atomic planes as represented by lines AB, CD, and EF in Fig. 1.12.

Assume two waves Y and Z of X-ray beams which are in phase fall on the surface of the crystal. If ray Y gets reflected from the first layer, i.e., AB line and ray Z is reflected from the second layer of atoms, i.e., CD line, then it is evident that as compared to ray Y, ray Z has to travel

a longer distance, equal to QRS in order to emerge out of the crystal. If waves Y and Z are in-phase (for the intensity of the reflected beam to be maximum) after reflection, the difference in distance travelled by the two rays must be equal to the integral multiple of wavelength, i.e., $n\lambda$ (for constructive interference).

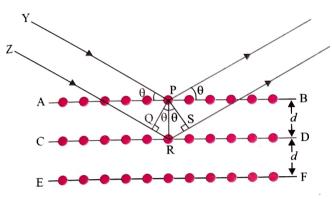


Fig. 1.12

Thus, distance QRS =
$$n\lambda$$
 ...(i)

It is obvious from the figure that $QR = RS = PR \sin \theta$

$$\therefore QRS = 2PR \sin \theta \qquad ...(ii)$$

If the distance between the successive atomic planes is d, then, PR = d. ...(iii)

So, from Eqs. (i), (ii), and (iii), we have

 $n\lambda = 2d \sin \theta$

This is Bragg's equation.

Thus, Bragg gave a mathematical equation to establish a relationship between the wavelength of the incident X-ray, the distance between the layers, and the angle of diffraction, where

 λ = wavelength of X-ray used.

 θ = angle between incident X-rays and the plane of the crystal. The diffracted beam makes an angle 2θ .

d = distance between planes of the constituent particles in a crystal.

n =an integer (1, 2, 3, 4, ...) which represents the serial order of diffracted beams.

For a given set of lattice planes, d has a fixed value. Therefore, the possibility of getting maximum reflection (i.e., the possibility of getting reflected waves in phase with one another) depends upon θ . If θ is increased gradually, a number of reinforced strong signals or positions will be found at which the reflections will be maximum. At these positions, n will have values equal to 1, 2, 3, Generally, in the experiments on X-ray reflections, n is set equal to 1. If λ is known, it is possible to determine d, the distances between atomic planes in the crystal by determining θ , experimentally. Similarly, if interplanar distances are given, the corresponding wavelengths of the incident beam of X-ray can be calculated.

ILLUSTRATION 1.1

A sample of a crystalline solid scatters a beam of X-rays of wavelength 70.93 pm at an angle 2θ of 14.66° . If this is a second-order reflection (n=2), calculate the distance between the parallel planes of atoms from which the scattered beam appears to have been reflected.

Sol.

We know that:
$$n\lambda = 2d \sin \theta$$

 $2\theta = 14.66^{\circ} \text{ or } \theta = 7.33^{\circ}$
 $\lambda = 70.93 \text{ pm} = 70.93 \times 10^{-12} \text{ m}$

$$\therefore d = \frac{n\lambda}{2\sin\theta} = \frac{2 \times 70.93 \times 10^{-12} \text{ m}}{2\sin 7.33^{\circ}} \text{ m}$$

$$= 556.3 \times 10^{-12} \text{ m}$$

$$= 556.3 \text{ pm}$$

ILLUSTRATION 1,2

Calculate λ of X-rays which give a diffraction angle $2\theta = 16.8^{\circ}$ for crystal, if the interplanar distance in the crystal is 0.2 nm and that only for the first-order diffraction is observed. Given $\sin 8.40^{\circ} = 0.146$.

Sol.

$$\lambda = \frac{2d \sin \theta}{n} = \frac{2 \times 0.20 \times 0.146}{1}$$
 (since $\theta = 8.40^{\circ}$)
= 0.584 nm
= 5.84 × 10⁻¹¹ m

1.7 LATTICE

Before discussing the periodic patterns of atomic arrangements in crystals, let us examine the arrangements of points in space in periodically repeating patterns. This leads us to the concept of a space lattice. A space lattice provides the framework with reference to which a crystal structure can be described.

Definition: It is the periodic arrangement of the points such that the environment at any point is the same as that at any other point. Every point in lattice should have same surroundings.

As an example, consider a two-dimensional square array of points shown in Fig. 1.13. By repeated translation of the two vectors a and b on the plane of the paper, we can generate the square array. The magnitudes of a and b are equal and can be taken to be unity. The angle between them is 90° ; a and b are called the fundamental translation vectors that generate the square array. To ignore end effects near the boundary, we will assume that the array can be extended infinitely. If we locate ourselves at any point in the array and look out in a particular direction that lies on the plane of paper, the scenery will be same, irrespective of where we are.

Consider the immediate surroundings of a point in the array. If we look due north or due east from this point we see another point at a distance of 1 unit. Along northeast, we see the nearest point at a distance of $\sqrt{2}$ units and along north-northeast, the nearest

point is at a distance of $\sqrt{2}$ units. As this is true of every point in the array, it satisfies the definition given above and can be called a two-dimensional square lattice.

The main features of a lattice are as follows:

- a. A lattice should be infinite.
- b. Each point in a lattice is called lattice point.
- **c.** Lattice points are joined by straight lines to represent the geometry of lattice.
- d. A lattice is different from a crystal. In fact a lattice gives rise to crystal when points are replaced by particles such as atoms, ion, or molecules.

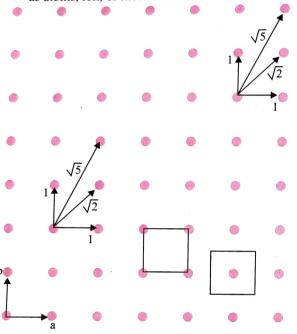
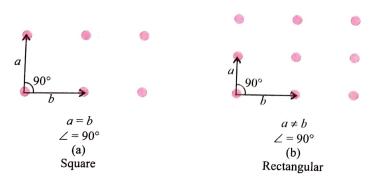


Fig. 1.13 Arrangement of points in space in periodically repeating pattern

1.7.1 FIVE TYPES OF TWO-DIMENSIONAL LATTICES

Space lattice is a regular repeating arrangement of points in space and forms the basis of the classification of all structures. For the sake of simplicity, let us understand the arrangement of points in two dimensions forming a two-dimensional lattice (Fig. 1.14).

There are five types of 2D-lattice (Fig. 1.14) which differ in the symmetry of the arrangement of points. They are: (a) hexagonal, (b) square, (c) rectangular, (d) rhombic, and (e) parallelogram.



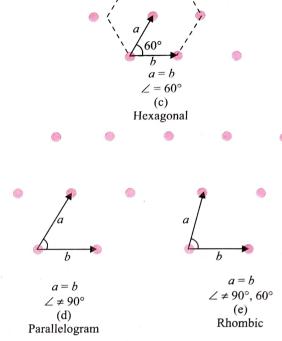


Fig. 1.14 Five types of 2-D lattice

Note: Pentagonal lattice is not possible because the interior angle of a regular pentagon is 108° which is not an integral factor of 360°.

A two-dimensional lattice is a regular arrangement of points. In order to specify it completely, only a small part of the lattice is described. Choose four points in a two-dimensional lattice and connect them to give a parallelogram. This figure is known as a unit cell.

A full lattice is generated by repeatedly moving the unit cell in the direction of its edges by a distance equal to the cell edge (Fig. 1.15).

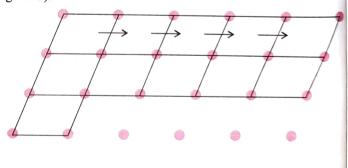


Fig. 1.15 Generation of an entire two-dimensional lattice by regular repetition of the unit cell in the direction of cell edges by distance equal to cell edge

For any lattice, a unit cell can be chosen in many different ways and may include any cell that has interior points. The smallest unit cell that shows the full symmetry of the lattice is most convenient.

The unit cells normally taken for square, rectangular, and parallelogram lattices are square, rectangle, and parallelogram, respectively. But for a hexagonal lattice, a rhombus with an angle of 60° is taken as the unit cell. However, a rectangular unit cell with an interior point is normally taken for the rhombic lattices.

A unit cell with an interior point is called a *centred unit cell*, in this case a centred rectangular unit cell. The unit cell that does not contain any interior point is known as *primitive unit cell*. Thus, for a two-dimensional lattice, a unit cell is specified by the length of its edges and the angle between them.

Note: For some lattices, the unit cell can be choosen in more than one way, as shown in Fig. 1.14(c). For the same lattice points, the unit cell may be a parallelogram, an equilateral triangle, or a regular hexagon with a lattice point in the centre.

In the first two unit cells, namely, parallelogram and equilateral triangle, all lattice points lie at the corners of the unit cell. Such unit cells are called "primitive unit cells." The third one, i.e., hexagon, in which one lattice point also lies at the centre, is known as "non-primitive unit cell."

The two-dimensional pattern is very common in the designs on many wallpapers and tiled floors. A complete two-dimensional pattern can be made by placing a motif (arrow) at a definite position at the lattice points (Fig. 1.16).

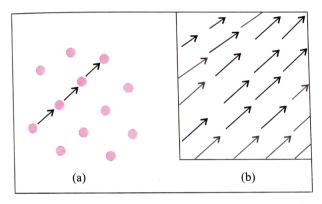
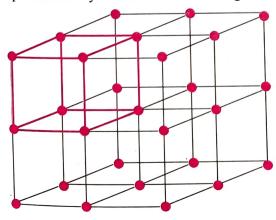


Fig. 1.16 Two-dimensional pattern

1.8 <u>CRYSTAL LATTICES AND UNIT</u> CELLS (3D)

The main characteristic of crystalline solids is a regular and repeating pattern of constituent practices. If the three-dimensional arrangement of constituent particles in the a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called *crystal lattice*. Thus, a regular three-dimensional arrangement of points in space is called a crystal lattice. A portion of a crystal lattice is shown in Fig. 1.17.



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Fig. 1.17 A portion of a three-dimensional cubic lattice and its unit cell

Just as there are five possible two-dimensional lattices, there are 14 possible three-dimensional lattices. These are called Bravais lattices (after the French mathematician who first described them). The following are the characteristics of a crystal lattice:

- a. Each point in a lattice is called lattice point or lattice site.
- **b.** Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms), or an ion.
- c. Lattice points are joined by straight lines to bring out the geometry of the lattice.
- **d.** Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions generates the entire lattice.

A unit cell is characterized by:

- **a.** Its dimensions along the three edges, a, b, and c. These edges may or may not be mutually perpendicular.
- **b.** angles between the edges: α (between b and c), β (between a and c), and γ (between a and b). Thus, a unit cell is characterized by six parameters, a, b, c, α , β , and γ . These parameters of a typical unit cell are shown in Fig. 1.18.

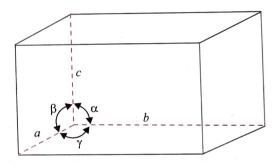


Fig. 1.18 Illustration of parameters of a unit cell

1.8.1 PRIMITIVE AND CENTRED UNIT CELLS

Unit cells can be broadly divided into two categories: primitive and centred unit cells.

Primitive Unit Cells

When constituent particles are present only on the corner positions of a unit cell, it is called as primitive unit cell.

Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. Centred unit cells are of three types:

- a. Body-centred units cells: Such a unit cell contains one constituent particle (atoms, molecule, or ion) at its body centre besides the ones that are at its corners [Fig. 1.19(b)].
- b. Face-centred unit cells: Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners [Fig. 1.19(c)].
- c. End-centred unit cell: In such unit cells, one constituent particle is present at the centre of any two opposite faces or alternative faces, besides the ones present at its corners [Fig. 1.19(d)].

In all, there are seven types of primitive unit cells and these seven crystal systems have 14 types of Bravais lattices (Tables). 1.14 Physical Chemistry

and 1.4) $T \equiv Top$ T $Bo \equiv Bottom$ $F \equiv Front$ Ba $Ba \equiv Back$ R L $R \equiv Right$ F $L \equiv Left$ Bo (d) End-centered (c) Face-centered (b) Body-centered (a) Simple or

Fig. 1.19 Types of primitive/centred unit cells on the basis of the presence of their constituent particles

1.8.2 SEVEN CRYSTAL SYSTEM

primitive

The crystallographers have been able to divide 32 point groups and 14 space lattices into seven crystal systems and 14 space or Bravais lattices. Their characteristics along with the central unit cells they can form have been listed in Table 1.3 and Figs. 1.20 and 1.21.

Table 1.3 Seven primitive unit cells and their possible variations as central unit cell

S.No.	Crystal system	Space or Bravais lattices lattices	Total Bravais elements length	Minimum symmetry or edge	Axial distance	Axial angles	Examples
1.	Cubic	Primitive Body-centred Face-centred	3	4 three-fold 3 four-fold	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$	NaCl, KCl ZnS, diamond, Cu
2.	Ortho- rhombic	Primitive Body-centred Face-centred End-centred 2-axis	4	Three mutually perpendicular 2-fold (or)	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	Rhombic sulphur, KNO ₃ BaSO ₄ , K ₂ SO ₄
3.	Tetragonal	Primitive Body-centred	2	1 four-fold axis of symmetry	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	White Sn, SnO
4.	Monoclinic	Primitive end-centred	2	1 two-fold axis of symmetry	$a \neq b \neq c$	$\alpha = \gamma = 90^{\circ}$ $\beta \neq 90^{\circ}$	NH ₄ Br Monoclinic sulphur, Na ₂ SO ₄ ·10H ₂ C
5.	Triclinic	Primitive	1	1 one-fold axis	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$	CaSO ₄ ·2H ₂ O
6.	Hexagonal	Primitive	1	of symmetry 1 six-fold axis	$a = b \neq c$		CuSO ₄ ,·5H ₂ O K ₂ Cr ₂ O ₇ , H ₃ BO
7.	Rhomo- bohedral	Primitive	1	of symmetry 1 three-fold		$\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$	Graphite, ZnO, CdS
	or Trigonal			axis of symmetry	a = b = c	$\alpha = \beta = \gamma \neq 90^{\circ}$	Calcite (CaCO; HgS (cinnabar) NaNO ₃ , ICl
_			Total = 14				3, 101

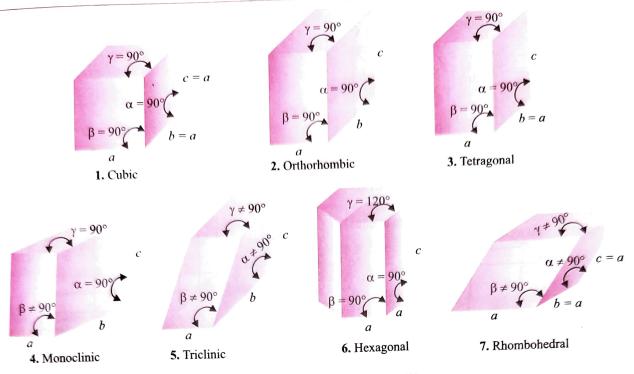
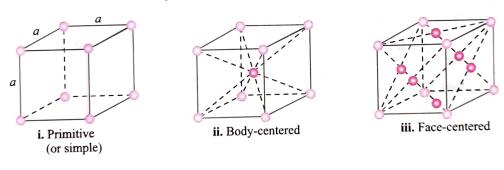
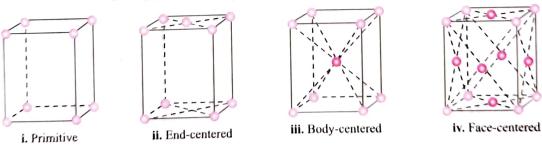


Fig. 1.20 Seven primitive unit cell in crystals

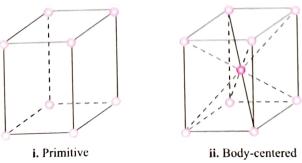
1. Cubic: All sides of same length between faces are all 90°



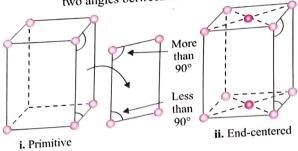
2. Orthorhombic: unequal sides, angles between faces all 90°



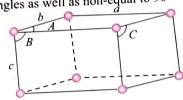
3. Tetragonal: one side different in length to the other, two angles between faces all 90°



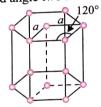
4. Monoclinic: one side different in length to the other, only two angles between faces are 90°



5. Triclinic: unequal sides a, b, c, and A, B, C are unequal angles as well as non-equal to 90°



6. Hexagonal: one side different in length to the other two, the marked angle two faces are 120°



7. Rhombohedral: All sides of equal length, only angles on two faces are 90°

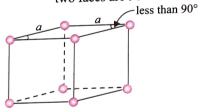


Fig. 1.21 Unit cells of 14 types of Bravais lattices

1.9 EFFECTIVE NUMBER OF ATOMS (Zeff) IN A UNIT CELL

A crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule, or ion). In a crystal, a particular atom located at a particular corner/face centre of a unit cell is shared by other cells and only a portion of such an atom actually lies within a given unit cell. The sum of all such portions of the shared atoms present under one unit cell gives effective number (Z_{eff}) of atoms in a given unit cell.

Consider three types of cubic unit cells taking constituent particle as atom.

a. Primitive cubic unit cell

A primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells as shown in Fig. 1.22, four unit cells in the same layer and

for unit cells of the upper (or lower) layer. Therefore, Only 1/8th of an atom actually belongs to a particular unit cell. Fig. 1.23, a primitive cubic unit cell has been shown in three different ways. Each small sphere in Fig. 1.23(a) represen only the centre of the particle occupying that position an not its actual size.

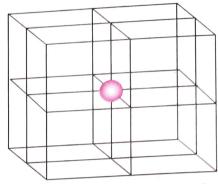


Fig. 1.22 In a simple cubic unit cell, each corner atom is shared between eight unit cells

Such structures are called open structures. The arrangement of particles is easier to follow in open structures. Figure 1.23(b) depicts the space-filling representation of a unit ce with actual particle size and Fig. 1.23(c) shows the actual portions of different atoms present in a cubic unit cell.

In all, since each cubic unit cell has 8 atoms on its corner the total number of atoms in one unit eight cell is 8x-= 1.

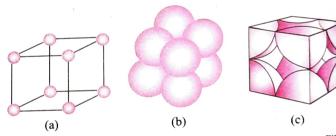
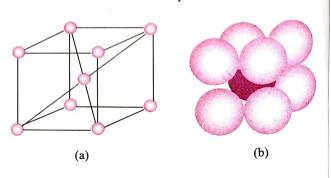


Fig. 1.23 A primitive cubic unit cell: (a) open structure, (b) space-filling structure, and (c) actual portions of atoms belonging to one unit cell

b. Body-centred cubic unit cell

A body-centred cubic (bcc) unit cell has an atom at each its corners and also one atom at its body centre. Figure 1.2 depicts (a) open structure, (b) space filling model, and the unit cell with portion of atoms actually belonging to it. can be seen that the atom at the body centre wholly belong to the unit cell in which it is present.



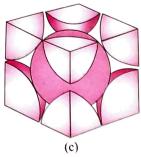


Fig. 1.24 A body-centred cubic unit cell: (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell

Thus, in a body-centred cubic (bcc) unit cell:

- i. 8 corners $\times \frac{1}{8}$ per corner atoms = $8 \times \frac{1}{8} = 1$ atom
- ii. 1 body centre atom = $1 \times 1 = 1$ atom
 - .: Total number of atoms per unit cell = 2 atoms

c. Face-centred cubic unit cell

A face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in Fig. 1.25(a) that each atom located at the face centre is shared between two adjacent unit cells and only half of each atom belongs to a unit cell. Figures 1.25(a)–1.25(d) depict open structure, space-filling model, and the unit cell with portions of atoms actually belonging to it, respectively. Thus, in a face-centred cubic (fcc) unit cell:

- i. 8 corners atoms $\times \frac{1}{8}$ atoms/unit cell = $8 \times \frac{1}{8}$
- ii. 6 face-centred atoms $\times \frac{1}{2}$ atom/unit cell = $6 \times \frac{1}{2}$ = 3 atoms

Total number of atom per unit cell = 4 atoms

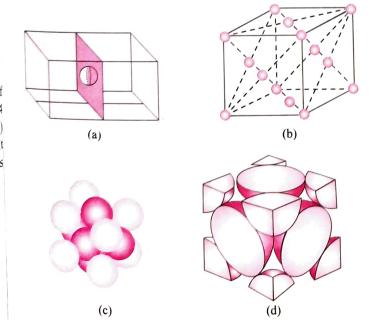


Fig. 1.25 A face-centred cubic unit cell: (a) An atom at face centre of unit cell is shared between two unit cells. (b) Open structure, (c) Space filling structure, (d) Actual portions of atoms belonging to one unit cells

d. Some other formulae

i. Total number of atoms in a unit cell

$$=\frac{n_{\rm c}}{8}+\frac{n_{\rm f}}{2}+\frac{n_{\rm b}}{1}+\frac{n_{\rm e}}{4}$$

where $n_c =$ Number of atoms at the corners of a unit cell

 n_f = Number of atoms at the centres of six faces of a unit cell

 n_b = Number of atoms completely inside the body of a unit cell

 n_e = Number of atoms at the edge centres of a unit cell

ii. Number of effective atoms at the alternate faces of unit

$$cell = \frac{2}{2} = 1$$

In a unit cell, there are only two alternate faces and each face-centred atom is shared between two unit cells and only half of each atom belongs to the unit cell.

∴ 2 face-centred atoms $\times \frac{1}{2}$ atoms per unit cell = 1 atom/unit cell.

Such type of arrangement of atoms is a unit cell is called end-centred system [refer Fig. 1.19(d)].

iii. Number of effective atoms at the alternate edge centres

of unit cell =
$$4 \times \frac{1}{4} = 1$$

In a unit cell, there are only four alternate edges and each edge-centred atom is shared between four unit cells and only 1/4th of each atom belongs to the unit cell (see Fig. 1.26).

∴ 4 edge-centred atoms $\times \frac{1}{4}$ atoms per unit cell = 1 atom/unit cell

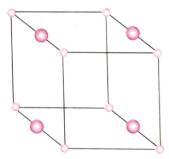


Fig. 1.26 Atoms at the alternative edge centres of a unit cell

iv. Number of body diagonals of a unit cell = 4/unit cell Number of face diagonals of a unit cell

- = 2 diagonals on each face
- $= 2 \times 6$ faces
- = 12/unit cell

Note:

a. Atoms on a body diagonal are inside the cube and they are not shared by any adjacent atoms.

b. Atoms on a face diagonal are shared by two unit cells and only 1/2 of each atom belongs to each unit cell.

Table 1.4 Number of atoms $(Z_{\rm eff})$ per unit cell

able 1.	.4 Number of atoms	(Z _{eff} / Pos			n _e	Effective atoms/unit cell
. No.	Cubic unit cell	n _c	n _f	n _b		8 corners $\times \frac{1}{8}$ per corner atom share = 1
	Simple cubic (sc)	8	0	0	0	Total effective atoms = 1/unit cell
	or primitive				0	Corner share $=\frac{1}{8} \times 8 = 1$
2.	Body-centred cubic (bcc)	8	0	1	0	Body-centred share = 1 Total effective atoms = $1 + 1 = 2$ /unit cell
3.	Face-centred cubic (fcc)	8	6	0	0	Corner share $= \frac{1}{8} \times 8 = 1$ Face-centred share $= 6 \times \frac{1}{2} = 3$
						Total effective atoms = $1 + 3 = 4$ /unit cell

ILLUSTRATION 1.3

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and Y atoms are at the face centres.

- a. Calculate: (i) Z_{eff}, (ii) total number of atoms in a cube, and (iii) formula of the compound.
- **b.** If all the atoms are removed from a single axis passing through the centre of the cube, calculate
 - (i) Z_{eff} , (ii) total number of atoms in a cube, and (iii) formula of the compound.

Sol

- a. i. Number of effective X atoms
 - = 8 corners $\times \frac{1}{8}$ per corner atom share
 - = 1 atom/unit cell

Number of effective Y atoms

- = 8 corners $\times \frac{1}{2}$ per face atom share
- = 3 atom/unit cell

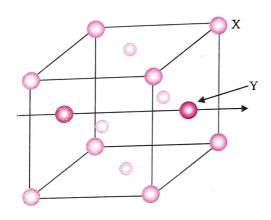
$$Z_{\text{eff (8X + Y)}} = 1 + 3 = 4$$

- ii. Total atoms in a cube
 - = 8X atoms at corner + 6Y atoms at faces.
 - = 8 + 6 = 14 atoms/unit cube
- iii. Formula of the compound:

$$Z_{\text{eff}(X)} = 1$$
, $Z_{\text{eff}(Y)} = 3$

Thus, formula of the compound = XY_3

b. i. Two atoms from two face centres are removed by passing an axis as shown in the figure below.



 \therefore Face centre atom left = 6 - 2 = 4

$$Z_{\text{eff(Y)}} = 4 \text{ Face atom} \times \frac{1}{2} \text{ per face atom share}$$

$$Z_{\text{eff(X)}} = 8 \text{ corners } \times \frac{1}{8} \text{ per corner atom share}$$

= 1 atom/unit cell

$$\therefore Z_{\text{eff}(X+Y)} = 2 + 1 = 3 \text{ atoms/unit cube.}$$

- ii. Total atoms in a cube = 8 (corners) + 4 (face centre) = 12 atoms/unit cube
- iii. Formula of the compound:

$$Z_{\text{eff(X)}} = 1$$
, $Z_{\text{eff(Y)}} = 2$

$$\therefore$$
 Formula = XY_2

ILLUSTRATION 1.4

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and two atoms (Y) are at each body diagonal of the cube.

- a. Calculate: (i) Z_{eff}. (ii) total number of atoms in a cube, and (iii) formula of the compound.
- b. If all atoms from one body diagonal of the cube except corners are removed, calculate: (i) Z_{eff} (ii) total number of atoms in the cube, and (iii) formula of the compound.

Sol.

a. i.
$$Z_{\text{eff}(X)}$$
 at corners = $\frac{1}{8} \times 8 = 1 = X$

 $Z_{\text{eff(Y)}}$ at body diagonal = 2 atoms × 4 body diagonal = 8 atoms/unit cell = 8 = Y $\therefore Z_{\text{eff(Y+Y)}} = 1 + 8 = 9$

Note: Body diagonal atoms are in the inner portion of the cubic unit cell and they are not shared with any adjacent atoms.

- ii. Total atoms in a cube = 8 (corners) + 8 (body diagonal)= 16 atoms/unit cube
- iii. Formula of the compound:

$$Z_{\text{eff(X)}} = 1, Z_{\text{eff(Y)}} = 8$$

Formula = XY_8

b. i. One body diagonal has 2Y atoms and they are removed.

$$Z_{\text{eff(Y)}}$$
 at body diagonal left = 8 - 2
= 6 atoms/unit cell

$$Z_{\text{eff(X)}}$$
 at corners = $8 \times \frac{1}{8} = 1 = X$
 $\therefore Z_{\text{eff(X+Y)}} = 6 + 1 = 7$ atoms/unit cell

- ii. Total atoms in a cube = 8 (corners) + 6 (body diagonal)
 = 14 atoms/unit cube
- iii. Formula of the compound:

$$Z_{\text{eff}(X)} = 1$$
, $Z_{\text{eff}(Y)} = 6$

Formula: XY₆

ILLUSTRATION 1.5

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and Y atoms are at the face centres. One atom X is missing from the corner.

- a. Calculate (i) Z_{eff} (ii) total number of atoms in the cube, and (iii) formula of the compound.
- b. If all the atoms are removed from one of the faces of the cube containing atoms at corners, as in (a) above, calculate (i) Z_{eff}, (ii) total number of atoms in a cube, and (iii) formula of the compound.

Sol.

a. i. Number of effective X atoms $= 7 \text{ corners} \times \frac{1}{8} \text{ per corner atom share}$ $= \frac{7}{8} \text{ atom/unit cell}$

Number of effective Y atoms = 6 faces $\times \frac{1}{2}$ per face atom share = 3 atoms/unit cell

$$Z_{\text{eff}(X+Y)} = \frac{7}{8} + \frac{3}{1} = \frac{.31}{8}$$

- ii. Total atoms in a cube = 7 (corner) + 6 faces = 13 atoms unit cube
- iii. Formula of the compound:

$$Z_{\text{eff}(X)} = \frac{7}{8}, \ Z_{\text{eff}(Y)} = 3$$

Thus, formula of the compound is $X_{\frac{7}{8}}Y_3$.

Simplifying: X₇Y₂₄.

b. i. Atoms removed from one face of the cube, containing all atoms at corners = 4 corners + 1
face-centred atom = 5 atoms/unit cell

Corner atom left = 7 - 4 = 3 atoms at corner Face-centre atom left = 6 - 1 = 5 atoms at face centre.

$$Z_{\text{eff(X)}} = 3 \text{ corner} \times \frac{1}{8} \text{ per corner atom share}$$

= $\frac{3}{8} \text{ atoms/unit cell}$

 $Z_{\text{eff(Y)}} = 5$ face-centred atom $\times \frac{1}{2}$ per face atom share $= \frac{5}{2}$ atoms/unit cell

ii. Total atoms in a cube = 3 (corner) + 5 (faces) = 8 atoms/unit cube

iii. Formula of compound:

$$Z_{\text{eff (X)}} = \frac{3}{8}, \ Z_{\text{eff (Y)}} = \frac{5}{2}.$$

Formula: $X_{\frac{3}{8}}Y_{5/2}$
Simplifying = $X_{3}Y_{20}$

ILLUSTRATION 1.6

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and also at the face centres. Y atoms are present at the body centre and at the edge centre of the cube.

a. Calculate (i) $Z_{\rm eff}$, (ii) total number of atoms in the cube, and (iii) formula of the compound.

- **b.** If all the atoms are removed from one of the body diagonals of the cube, calculate (i) $Z_{\rm eff}$, (ii) total number of atoms in the cube, and (iii) formula of the compound.
- c. If all the atoms from the diagonals of one of the face of the cube are removed, calculate (i) Z_{eff}, (ii) total number of atoms in the cube, and (iii) formula of the compound.
- d. If all the atoms are removed from one of the plane passing through the middle of the cube, calculate
 (i) Z_{eff} (ii) total number of atoms in the cube, and
 (iii) formula of the compound.
- e. If all the atoms are removed from one of the axes passing through one of the face centres of the cube, calculate
 (i) Z_{eff} (ii) total number of atoms in the cube, and
 (iii) formula of the compound.

Sol.

a. i.
$$Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4$$

$$z_{\text{eff(Y)}} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{1}{1} + \frac{12}{4} = 1 + 3 = 4.$$

$$Z_{\text{eff}(X+Y)} = 4 + 4 = 8$$

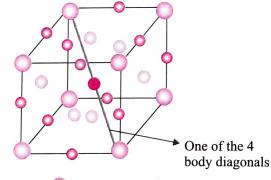
ii. Total number of atoms in the cube

$$= 8 \text{ (corner)} + 6 \text{ (face centre)} + 1 \text{ (body centre)}$$

iii. Formula:
$$Z_{\text{eff}(X)} = 4$$
, $Z_{\text{eff}(Y)} = 4$

$$\Rightarrow X_{\Delta}Y_{\Delta} = 4XY$$

b. i.



$$X \Rightarrow \bigcirc = 8$$
 corner atoms

$$Y \Rightarrow \bigcirc = 1$$
 body center atom

$$Y \Rightarrow \bigcirc = 12$$
 edge center atoms

$$X \Rightarrow \bigcirc = 6$$
 face center atoms

Atoms removed from one body diagonal

$$= 3$$
 atoms.

$$Z_{\text{eff(X)}} = \frac{n_{\text{c}}}{8} + \frac{n_{\text{f}}}{2} = \frac{(8-2)}{8} + \frac{6}{2} = \frac{15}{4}$$

$$Z_{\text{eff(Y)}} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{(1-1)}{1} + \frac{12}{4} = 0 + 3 = 3$$

$$Z_{\text{eff}(X+Y)} = \frac{15}{4} + 3 = \frac{27}{4}$$

ii. Total number of atoms in the cube

= 6 (corner) + 6 (face centre) + Zero (
$$b_{0dy}$$

centre) + 12 (edge c_{entra}

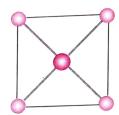
= 24 atoms/unit cube

iii.
$$Z_{\text{eff}(X)} = \frac{15}{4}$$
, $Z_{\text{eff}(Y)} = 3$

$$\Rightarrow X_{\frac{15}{4}} Y_3.$$

Simplifying X₁₅Y₁₂

c. i.



 $X \Rightarrow \bigcirc = 4$ corner atoms are removed

 $X \Rightarrow \bigcirc = 1$ face center atom is removed

$$Z_{\text{eff(X)}} = \frac{n_{\text{c}}}{8} + \frac{n_{\text{f}}}{2} = \frac{(8-4)}{8} + \frac{(6-1)}{2} = \frac{1}{2} + \frac{5}{2} = 3$$

$$Z_{\text{eff(Y)}} = \frac{n_b}{1} + \frac{n_e}{4} = \frac{1}{1} + \frac{12}{4} = 1 + 3 = 4$$

$$Z_{\text{eff}(X+Y)} = 3 + 4 = 7$$

ii. Total number of atoms in a cube

$$= 4 \text{ (corner)} + 5 \text{ (face centre)} + 1 \text{ (body centre)}$$

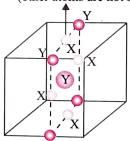
+ 12 (edge centre

= 22 atoms/unit cube

iii. Formula:
$$Z_{eff(X)} = 3$$
, $Z_{eff(Y)} = 4$

$$\Rightarrow X_3Y_4$$
.

d. Plane passing through the middle of cube (other atoms are not shown)



 $Y \Rightarrow \bigcirc = 1$ body center atom is removed

$$Y \Rightarrow \bigcirc = 4$$
 edge center atoms are removed

$$X \Rightarrow \bigcirc = 4$$
 face center atoms are removed

i.
$$Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{8}{8} + \frac{6-4}{2} = 1+1=2$$

$$Z_{\text{eff(Y)}} = \frac{n_{\text{b}}}{8} + \frac{n_{\text{e}}}{4} = \frac{(1-1)}{1} + \frac{(12-4)}{4} = 2.$$

$$Z_{\text{eff}(X+Y)} = 2 + 2 = 4$$

ii. Total number of atoms in the cube

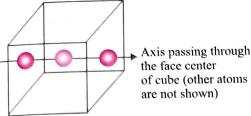
= 8 (corner) + 2 (face centres) + zero (body)centre) + 8 (edge centres)

= 18 atoms/unit cube

iii. Formula: $Z_{eff(X)} = 2$, $Z_{eff(Y)} = 2$

Formula is $X_2Y_2 = 2XY$.

e.



 $Y \Rightarrow \bigcirc = 1$ body center atom is removed

 $X \Rightarrow \bigcirc = 2$ face center atoms are removed

i.
$$Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{8}{8} + \frac{(6-2)}{2} = 1 + 2 = 3.$$

$$Z_{\text{eff}(Y)} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{(1-1)}{1} + \frac{12}{4} = 0 + 3 = 3.$$

$$Z_{\text{eff}(X+Y)} = 3 + 3 = 6.$$

ii. Total number atoms in a cube

= 8 (corner) + 6 (face centre)

zero (body centre) + 12 (edge centre)

= 24 atoms/unit cube

iii. Formula: $Z_{\text{eff}(X)} = 3$, $Z_{\text{eff}(Y)} = 3$

Formula is X_3Y_3 or 3XY.

ILLUSTRATION 1.7

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and also at alternate face centres. Y atoms are present at the body centre and also at the alternate edge centre of the cube.

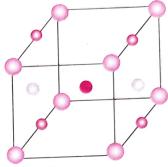
- a. Calculate (i) $Z_{\rm eff}$ (ii) total number of atoms in the cube, and (iii) formula of the compound.
- b. If all the atoms are removed from one of the plane passing through the middle of the cube which contains atoms both on the edge centre as well as on the face centre, calculate (i) $Z_{\rm eff}$ (ii) total number of atoms in the cube, and (iii) formula of the compound.
- c. If all the atoms are removed from one of the plane passing through the middle of the cube which contains atoms only on the edge centre but not on face centre, calculate (i) \mathbf{Z}_{eff} (ii) total number of atoms in the cube, and (iii) formula of the compound.
- d. If all the atoms are removed from one of the plane passing through the middle of the cube which neither contains atoms on the edge centre nor on the face centre, calculate (i) Z_{eff}, (ii) total number of atoms in the cube,

and (iii) formula of the compound.

- e. If all the atoms are removed from one of the axes passing through the middle of the cube containing face centre atoms, calculate (i) $Z_{\rm eff}$ (ii) total number of atoms in a cube, and (iii) formula of the compound.
- f. If all the atoms are removed from one of the axes passing through the middle of the cube not containing face centre atoms, calculate (i) $Z_{\rm eff}$ (ii) total number of atoms in the cube, and (iii) formula of the compound.

Sol.

a. i.



 $X \Rightarrow \bigcirc = 8 \text{ corner atoms}$

 $X \Rightarrow \bigcirc = 2$ alternate face center atoms

 $Y \Rightarrow \bigcirc = 4$ alternate edge center atoms

 $Y \Rightarrow \bigcirc = 1$ body center atom

$$Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{\text{Alternate } n_f}{2} = \frac{8}{8} + \frac{2}{2} = 1 + 1 = 2$$

$$Z_{\text{eff(Y)}} = \frac{n_b}{1} + \frac{\text{Alternate } n_e}{4} = \frac{1}{1} + \frac{4}{4} = 1 + 1 = 2$$

$$Z_{\text{eff}(X+Y)} = 2 + 2 = 4$$

ii. Total number of atoms in a cube

= 8 (corner) + 2 (alternate face centre)

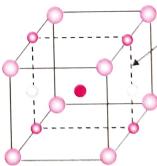
+ 4 (alternate edge centre) + 1 (body centre)

= 15 atoms/unit cube

iii. Formula: $Z_{\text{eff}(X)} = 2$, $Z_{\text{eff}(Y)} = 2$

 \therefore Formula = $X_2Y_2 = 2XY$

b. i.



Plane passing through the middle of the cube containing atoms both on edge center and face center

 $X \Rightarrow \bigcirc = 2 X$ atoms from face center are removed

 $Y \Rightarrow \bigcirc = 4 \text{ Y atoms from edge center are removed}$

 $Y \Rightarrow \bullet = 1 \text{ Y atom from body center is removed}$

$$Z_{\text{eff(X)}} = \frac{n_c}{8} + \frac{\text{Alternate } n_f}{2} = \frac{8}{8} + \frac{(2-2)}{2}$$

= 1 + 0 = 1

$$Z_{\text{eff(Y)}} = \frac{n_b}{1} + \frac{\text{Alternate } n_c}{4} = \frac{(1-1)}{1} + \frac{(4-4)}{4}$$

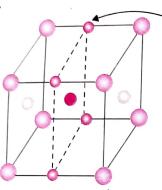
= 0 + 0 = zero

$$Z_{\text{eff}(X+Y)} = 1 + 0 = 1$$

- ii. Total number of atoms in a cube
 - = 8 (corner) + zero (body centre) + zero (face centre)
 - + zero (edge centre)
 - = 8 atoms/unit cube
- iii. Formula: $Z_{\text{eff}(X)} = 1$, $Z_{\text{eff}(Y)} = \text{zero}$

$$\therefore$$
 Formula = X

c. i.



Plane passing through middle of the cube containing atoms only on the edge center

$$Y \Rightarrow \bigcirc = 4 \text{ Y atoms from edge center}$$
 are removed

$$Y \Rightarrow \bullet = 1 \text{ Y atom from body center is}$$
 removed

$$Z_{\text{eff(X)}} = \frac{n_{\text{c}}}{8} + \frac{n_{\text{f}} \text{ (Alternate)}}{2} = \frac{8}{8} + \frac{2}{2}$$

$$= 1 + 1 = 2$$

$$Z_{\text{eff(Y)}} = \frac{n_{\text{b}}}{1} + \frac{n_{\text{e}} \text{ (Alternate)}}{4} = \frac{(1-1)}{1} + \frac{(4-4)}{4}$$

$$= 0 + 0 = 0$$

$$Z_{\text{eff}(X+Y)} = 2 + 0 = 2$$

ii. Total number of atoms in a cube

+ zero (body centre)

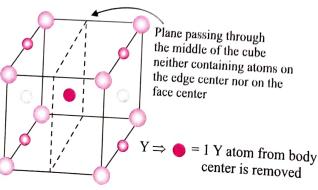
+ zero (alternate edge centre)

= 10 atoms/unit cube

iii. Formula:
$$Z_{eff(X)} = 2$$
, $Z_{eff(Y)} = Zero$

Formula =
$$X_2$$

d. i.



:
$$Z_{\text{cff(X)}} = \frac{n_{\text{c}}}{8} + \frac{\text{(Alternate)} \ n_{\text{f}}}{2} = \frac{8}{8} + \frac{2}{2}$$

= 1 + 1 =

$$Z_{\text{eff (Y)}} = \frac{n_b}{1} + \frac{\text{(Alternate) } n_e}{4} = \frac{(1-1)}{1} + \frac{(4)}{4}$$

= 0 + 1 = 1

$$Z_{\text{eff}(X+Y)} = 2 + 1 = 3.$$

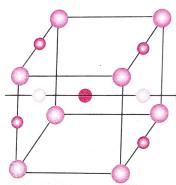
ii. Total number of atoms in a cube

(body centre

= 14 atoms/unit cube
iii. Formula:
$$Z_{eff(X)} = 2$$
, $Z_{eff(Y)} = 1$

$$\therefore$$
 Formula = X_2Y

e. i.



Axis passing through the middle of the cube containing face center atoms

 $Y \Rightarrow \emptyset = 1$ Y atom from body center is removed

 $X \Rightarrow \bigcirc = 2 X$ atoms from face center are removed

$$\therefore Z_{\text{eff(X)}} = \frac{n_{\text{c}}}{8} + \frac{\text{Alternate } n_{\text{f}}}{2} = \frac{8}{8} + \frac{(2-2)}{2}$$
$$= 1 + 0 = 1$$

$$Z_{\text{eff(Y)}} = \frac{n_b}{1} + \frac{\text{alternate}(n_e)}{4} = \frac{(1-1)}{1} + \frac{4}{4}$$

= 0 + 1 = 1

$$Z_{\text{eff}(X+Y)} = 1 + 1 = 2$$

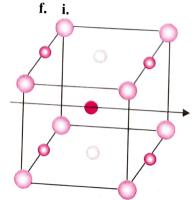
ii. Total number of atoms in a cube

= 8 (corner) + 4 (edge centre) + zero (body centre)

+ zero (face centre) = 12 atoms/unit cube.

iii. Formula:
$$Z_{\text{eff}(X)} = 1$$
, $Z_{\text{eff}(Y)} = 1$.

$$\therefore$$
 Formula = XY.



Axis passing through the middle of the cube not containing face center atoms

T be

 $Y \Rightarrow \bullet = 1$ Y atom from body center is removed

$$Z_{\text{eff(Y)}} = \frac{n_b}{1} + \frac{\text{Alternate } n_e}{4} = \frac{(1-1)}{1} + \frac{4}{4}$$

= 0 + 1 = 1

$$Z_{\text{eff}(X+Y)} = 2 + 1 = 3$$

ii. Total number of atoms in a cube

$$= 8 \text{ (corner)} + 2 \text{ (face centre)}$$

= 14 atoms/unit cube

iii. Formula:
$$Z_{\text{eff}(X)} = 2$$
, $Z_{\text{eff}(Y)} = 1$

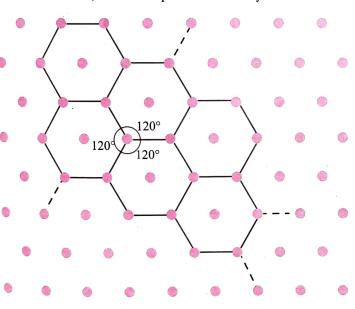
$$\therefore$$
 Formula = X_2Y

ILLUSTRATION 1.8

Draw a two-dimensional hexagonal lattice. Try to visualize the possibility of pentagonal two-dimensional lattice.

Sol.

Three regular hexagons intersect at one point. So, in this twodimensional lattice, this lattice point is shared by three unit cells.



So, the effective number of lattice points per unit cell $= 6 \times \left(\frac{1}{3}\right) + 1 \times (1) = 3.$

A regular pentagon has an interior angle of 108°. As 360° is not an integral multiple or 108°, pentagons cannot be made to meet at a point bearing a constant angle to one another. Hence, a pentagonal lattice is not possible. On the other hand, a square or a hexagonal two-dimensional lattice is possible as their internal angles add up to give 360°.

1.10 ATOMIC RADIUS AND SHORTEST DISTANCES IN CUBIC SYSTEM

The atomic radius is defined as half the distance (centre to centre) between the neighbouring atoms in a crystal. It is expressed in terms of edge a of the unit cell of a crystal.

a. Simple cubic (sc)

Each corner atom is in contact with its corner atoms as i Fig. 1.27.

$$2r = a \Rightarrow r = \frac{a}{2}$$

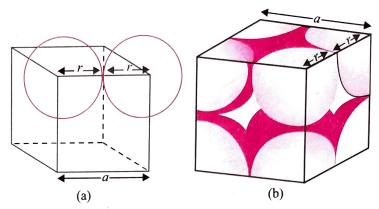


Fig. 1.27 (a) Atomic radius of a simple cube and (b) actual portions of atoms in an sc unit cell

b. Body-centred cubic (bcc)

Each corner of the unit cell touches the body centre atom (not corner atoms) such that

$$2r = \frac{\sqrt{3}}{2}a$$

$$r = \frac{\sqrt{3}}{4}a$$

Alternatively

From Fig. 1.28(a), it is clear that

$$(AC)^2 = (AB)^2 + (BC)^2 = a^2 + a^2 = 2a^2$$

$$(AD)^2 = (AC)^2 + (DC)^2$$

$$(4r)^2 = 2a^2 + a^2$$

$$16r^2 = 3a^2$$

$$\therefore r = \frac{\sqrt{3}}{4}a$$

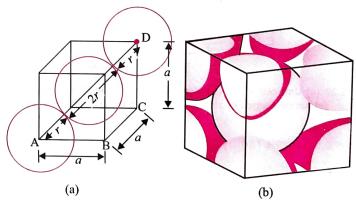


Fig. 1.28 (a) Atomic radius of a bcc and (b) actual portion of atoms in a bcc unit cell

c. Face-centred cubic (fcc)

Each corner of a particular face centre atom touches the other face centre atom (not corner atom) such that

$$2r = \frac{a}{\sqrt{2}} \implies r = \frac{a}{2\sqrt{2}}$$

Alternatively

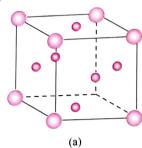
From Fig. 1.29(b), it is clear that

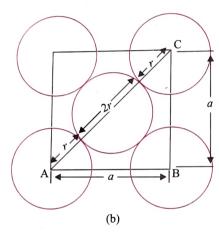
$$(AC)^2 = (AB)^2 + (BC)^2$$

$$(4r)^2 = a^2 + a^2$$

$$16r^2 = 2a^2$$

$$\therefore r = \frac{a}{2\sqrt{2}}$$





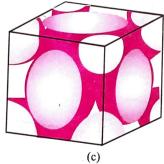


Fig. 1.29 (a) Unit cell of fcc, (b) view of one face of an fcc unit cell, and (c) actual portion of atoms belonging to the fcc unit cell

Table 1.5 Atomic radius of the atoms in different cubic systems

S.No.	Cubic unit cell	Atomic radius
1.	Simple cubic	r = a/2
2.	Body-centred cubic (bcc)	$16r^2 = 3a^2 \Rightarrow r = \frac{\sqrt{3}}{4}a = 0.433a$
3.	Face-centred cubic (fcc)	$16r^2 = 2a^2 \Rightarrow r = \frac{a}{2\sqrt{2}} = 0.3535a$

1.11 COORDINATION NUMBER (CN)

The number of atoms in a crystal which surround a particular atom as its nearest neighbour atoms in its neighbourhood is called its coordination number.

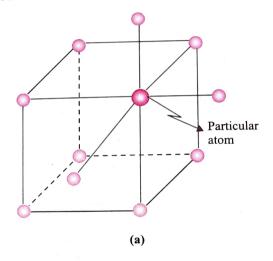
Note:

- a. For diatomic atoms, coordination number of cations is the number of surrounding anions or vice-versa.
- b. In crystals with directional bonds, coordination number is lower than that of crystals with non-directional bonds such as metals and ionic compounds.

The coordination number of monoatomic crystals is discussed below.

a. Simple cubic (sc)

Coordination number = 6.

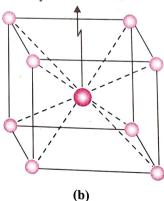


b. Body-centred cubic (bcc)

Number of atoms surrounding (touching) the body centratom = 8

Hence, coordination number = 8

Body-centered atom is surrounded by 8 corner atoms



c. Face-centred cubic (fcc)

Number of atoms surrounding (touching) the face centrof any face = 12

Hence, coordination number = 12

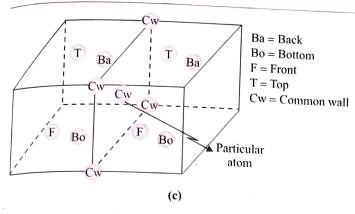


Fig. 1.30 (a) CN in sc (b) CN in bcc (c) CN in fcc

Table 1.6 Coordination number of different cubic systems

S. No.	Cubic unit cell	Coordination number (CN)
1.	Simple cubic (sc)	6
2.	Body-centred cubic (bcc)	8
3.	Face-centred cubic (fcc)	12

1.12 PACKING FRACTION (PF) OR SPACE OCCUPIED BY ATOMS IN A CUBIC SYSTEM

It is the ratio of the volume occupied by the total effective atoms in $Z_{\rm eff}$ in a cubic system to the volume of the unit cell.

Packing fraction =
$$\frac{\text{Volume occupied by effective atoms}}{\text{Volume of the unit cell}}$$
$$= \frac{Z_{\text{eff}} \times \text{Volume of atom}}{a^3} \times 100$$
$$= \frac{Z_{\text{eff}} \times \frac{4}{3} \pi r^3}{a^3}$$

Packing efficiency =
$$\frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}} \times 100$$

= $\frac{Z_{\text{eff}} \times \text{Volume of atom}}{a^3} \times 100$

a. Simple cube (sc)

Suppose the edge length of a unit cell = a and radius of the sphere = r

$$Z_{\text{eff}} = 1 \text{ atom/unit cell}$$

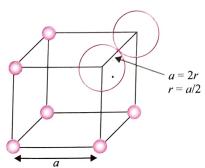


Fig. 1.31 PF in sc

As spheres are touching each other, evidently, $r = \frac{a}{2}$

Number of spheres per unit cell = $\frac{1}{8} \times 8 = 1$

Volume of the sphere = $\frac{4}{3} \pi r^3$

Volume of the cube = a^3

Packing fraction (PF) = $\frac{Z_{\text{eff}} \times \text{Volume of sphere}}{a^3}$

$$= \frac{1 \times \frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi \left(\frac{a}{2}\right)^3}{a^3}$$
$$= \frac{\pi}{6} = 0.524$$

Packing efficiency = % space occupied = 52.4%% empty space = 100 - 52.4= 47.6%

b. Body-centred cubic (bcc)

As the sphere at the centre touches the corner spheres (but corner spheres are not touching each other).

 $Z_{\rm eff} = 2$ atoms/unit cell

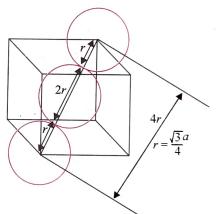


Fig. 1.32 PF in bcc

From section 1.10(b), $r = \frac{\sqrt{3}}{4} a$

$$PF = \frac{Z_{\text{eff}} \times \frac{4}{3} \pi r^3}{a^3} \qquad \dots (i)$$

Substitute the value of r in Eq. (i),

$$PF = \frac{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{4} a\right)^3}{a^3} = \frac{\sqrt{3}}{8} \pi = 0.68$$

% space occupied = 68% % empty space = 100 - 68 = 32%

c. Face-centred cubic (fcc)

As the spheres on the faces are touching each other (but corner atoms are not touching each other)

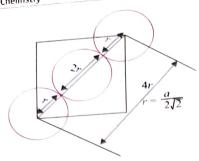


Fig. 1.33 PF in fcc

From section 1.10(c),
$$r = \frac{a}{2\sqrt{2}}$$

$$PF = \frac{Z_{\text{eff}} \times \frac{4}{3} \pi r^3}{a^3}$$

Substitute the value of r in Eq. (i),

$$PF = \frac{4 \times \frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3}$$
$$= \frac{\sqrt{2}}{6} \pi = 0.7404$$

% occupied = 74.04%

% empty space ≈ 36%

Table 1.7 Packing fraction of different cubic systems

S.No.	Cubic unit cell	Packing fraction (PF)	Packing efficiency (%)
1.	Simple cubic (sc)	$PF = \frac{\pi}{6} = 0.524$	52.4
2.	Body-centred cubic (bcc)	$PF = \frac{\sqrt{3}}{8}\pi = 0.68$	68
3.	Face-centred cubic (fcc)	$PF = \frac{\sqrt{2}}{6}\pi = 0.74$	74

Note:

An fcc unit cell occupies maximum space and hence it is referred as a close packed system.

1.13 CALCULATION OF THE DENSITY OF A METAL BY USING UNIT CELL DIMENSIONS

From the unit cell dimensions, the volume of a unit cell can be calculated. Similarly, from the density of a metal, the mass of the atoms in a unit cell can be calculated. The determination of the mass of a single atom provides an accurate method of determination of Avogadro's constant.

Let a be the edge length of a unit cell of a cubic crystal determined by X-ray diffraction method, ρ be the density of the solid substance, and Mw be the molar mass.

Thus, for a cubic crystal

Volume of unit cell =
$$a^3$$

= $(a \text{ pm})^3$
= $(a \times 10^{-10} \text{ cm})^3$
= $a \times 10^{-30} \text{ cm}^3$

1 pm = 10^{-12} m = 10^{-10} cm.

...(i)

Mass of unit cell = Number of atoms in unit cell (Z_{eff})

× Mass of each atom (...

$$=Z_{\mathrm{eff}} \times m$$

Mass of an atom present in the unit cell is given by:

Mass of an atom present in and
$$Mw = Molar mass$$

$$m = \frac{Mw}{N_A} \qquad \qquad M_A = Avogadro's constant$$

Therefore, the density of the unit cell is:

$$\rho = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{Z_{\text{eff}} \times m}{a^3 \times 10^{-30}} = \frac{Z_{\text{eff}} \times Mw}{a^3 \times N_A \times 10^{-30}} \text{ g cm}^{-3}$$

If M_W is in g mol⁻¹, then a^3 must be taken in cm³.

In terms of SI units, Mw is given in kg mol⁻¹, then a^3 must taken in m3.

Then,
$$\rho = \frac{Z_{\text{eff}} \times Mw}{N_{\text{A}} \times a^3} \text{ kg m}^{-3}$$

The density of the substance is same as the density of the un cell. The above equation involves five parameters. Knowing an four, the fifth can be calculated.

Table 1.8 Densities of cubic systems

s. No.	No. Cubic unit cell		Density (p) (g cm ⁻³)	
1.	Simple cubic (sc)	Z _{eff}	$\rho = \frac{1 \times Mw}{N_A \times a^3 \times 10^{-30}}$	
2.	Body-centred cubic (bcc)	2	$\rho = \frac{2 \times Mw}{N_A \times a^3 \times 10^{-30}}$	
3.	Face-centred cubic (fcc)	4	$\rho = \frac{4 \times Mw}{N_A \times a^3 \times 10^{-30}}$	

Alternatively (for monoatomic crystal)

Density is defined as the ratio of mass of unit cell and volume unit cell.

Init cell.

$$\rho = \frac{\text{Mass of atoms present in unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{(Z_{\text{eff}}) \times (Mw \text{ in amu})}{6.023 \times 10^{23} \times \dot{a}^3} \left[\frac{1}{6.023 \times 10^{23}} = 1.67 \times 10^{23} \right]$$

$$= \frac{(Z_{\text{eff}} \times Mw \text{ in amu}) \times 1.67 \times 10^{-24} \text{ g}}{a^3}$$

$$= \frac{(Z_{\text{eff}} \times Mw \text{ in amu}) \times 1.67 \times 10^{-27} \text{ kg}}{a^3}$$

In general,

(m)

be

iit

1**y**

 Σ (Number of atoms of each kind)

$$\rho = \frac{\times (Mw \text{ of each kind in amu}) \times 1.67 \times 10^{-27} \text{ kg}}{a^3}$$

(Number of formula units)

or
$$\rho = \frac{\times (Mw \text{ of the compound}) \times 1.67 \times 10^{-27} \text{ kg}}{a^3}$$

Table 1.9 Summary of various characteristics of different cubic systems

S. No.	Cubic unit cell	Number of effective atoms per unit cell (Z_{eff})	Coordination number (CN)	Atomic radius (r)	Packing efficiency	Density (ρ) (g cm ⁻³)	Nearest neighbour distance (d)
1.	Simple cube	1	6	$r=\frac{a}{2}$		$\rho = \frac{Z_{\text{eff}} \times Mw}{N_{\text{A}} \times a^3 \times 10^{-30}}$	а
	(sc)				= 52.36%	$= \frac{1 \times Mw}{N_{\rm A} \times a^3 \times 10^{-30}}$	
2.	Body-centred cubic (bcc)	2	8	$r = \frac{\sqrt{3}}{4}a$	$PE = \frac{\sqrt{3}}{8} \pi \times 100$ $= 68 \%$	$\rho = \frac{2 \times Mw}{N_A \times a^3 \times 10^{-30}}$	$\frac{\sqrt{3}}{2}a$
3.	Face-centred cubic (fcc	4	12	$r = \frac{a}{2\sqrt{2}}$	$PE = \frac{\sqrt{2}}{6} \pi \times 100$ = 74.04%	$\rho = \frac{4 \times Mw}{N_{\rm A} \times a^3 \times 10^{-30}}$	$\frac{a}{\sqrt{2}}$

ILLUSTRATION 1.9

Consider the parallelograms shown in the figure (i) representing two-dimensional unit cells.

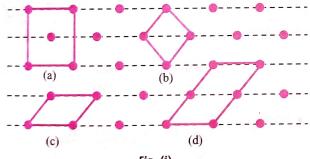


Fig. (i)

- a. What is the content of the unit cell as shown in figure (i)?
- b. In Fig. (i) which of these are primitive and which are multiple unit cells? Are any of these orthogonal?
- c. How many nearest neighbour circles does a given circle have in the figure (ii)?
- **d.** What is the relation between the radius of circle and the length of parallelogram for the unit cell shown in the figure below (space filling diagram)?



Fig. (ii)

- e. What is the packing fraction of the unit cell in the figure (ii)?
- **f.** What is the radius of the triangular hole shown in the figure (ii)?

Sol.

a. The unit cell content (*Z*) is the total number of atoms contained within the unit cell. From the (b) in Fig. (ii), only part of each circle at each corner is contained within the parallelogram unit cell.

Note: Remember it is a 2D unit cell.

Each circle is touching 4 other circles, so share of each circle is $\frac{1}{4} \Rightarrow Z = \frac{1}{4} \times 4 = 1$.

- **b.** Primitive unit cells are (b) and (c), because the only points contained in the unit cell are at the corners of the parallelograms.
 - Unit cell (a) and (d) are multiple unit cells because there are points in the unit cells in addition to the corners of the parallelogram.
 - Unit cell (a) is an orthogonal unit cell because it contains angles of 90°.
- c. The crystal coordination number (CN) is the number of nearest neighbours around a given atom, ion, or molecule in the crystal.
 - From the first figure (i), each atom (except the "surface" atom) is touching 6 other atoms, so CN = 6.
- **d.** a = 2R, where a is the length of the side of parallelogram and R is the radius of circle.
- e. Packing fraction = $\frac{\text{Area occupied by circles}}{\text{Area of unit cell}}$ Since Z = 1, area of circle = πR^2

Area of parallelogram = $2\sqrt{3}R^2$

$$\therefore PF = \frac{Z \times \pi R^2}{2\sqrt{3}R^2} = \frac{\pi}{2\sqrt{3}} = 0.907$$

f. (Refer section 1.15.2).
Let R is the radius of larger circle and r is the radius of the triangular hole:

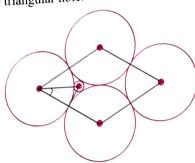


Fig. (iii)

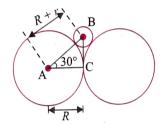


Fig. (iv)

In
$$\triangle ABC$$
, $\cos 30^{\circ} = \frac{Base}{Hypotenuse} = \frac{AC}{AB} = \frac{R}{R+r}$,
 $\Rightarrow (R+r)\cos 30^{\circ} = R$.
 $\Rightarrow r = \left(\frac{2}{\sqrt{3}} - 1\right)R$

ILLUSTRATION 1.10

Why uncharged atoms or molecules never crystallize in simple cubic structures?

Sol. Uncharged atoms and molecules pack more effectively in close-packed structures. Thus they never crystallises in simple cubic structures.

ILLUSTRATION 1.11

Why an end-centred unit cell cannot be cubic? What is the minimum possible symmetry for this type of unit cell?

Sol. A cubic unit cell must have all the six faces the same. But for end centered unit cell, $a \ne b \ne c$. Thus minimum symmetry possible for an end centred unit cell is orthorhombic or monoclinic..

ILLUSTRATION 1.12

Why a hexagonal close-packed structure and a cubic close-packed structure for a given element would be expected to have the same density?

Sol. The two structures have the same coordination number, hence the same packing efficiency.

1.14 CLOSE-PACKED STRUCTURES

In order to understand the packing of the constituent particles in a crystal, it is assumed that the constituent particles are identical hard spheres. The constituent particles in solids are close packed in such a way that they occupy maximum available space leaving minimum vacant space, and hence the crystal has maximum density. The building of these identical hard spheres in a three dimensional structure occurs in three steps:

a. Close packing in one dimension

There is only one way of arranging spheres in a one dimensional close-packed structure, that is, to arrange them in a row touching each other (Fig. 1.34).

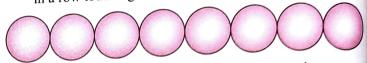


Fig. 1.34 Close packing of spheres in one dimension

In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its coordination number. Thus, in one-dimensional close-packed arrangement, the coordinate number is 2.

b. Close packing in two dimensions

A two-dimensional close-packed structure can be constructed by stacking (placing) the rows of close-packed spheres. This can be done in two different ways.

i. The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as "A" type row, the second row being exactly the same as the first one, is also of "A" type. Similarly, we may place more rows to obtain AAA type of arrangement as shown in Fig. 1.35 (a).

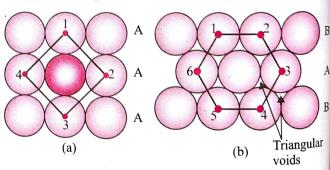


Fig. 1.35 (a) Square close packing and (b) hexagonal close packing in two dimensions

In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two-dimensional coordination number is 4. Also, if the centres of these four immediate neighbouring spheres are joined, a square is formed. Hence, this packing is called *square close packing in two dimensions*. But this type of packing is not efficient as more vacant space is left by the spheres in this arrangement.

ii. The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first two. If the arrangement of

spheres in the first row is called "A" type, the one in the second row is different and may be called "B" type. When the third row is placed adjacent to the second in a staggered manner, its spheres are aligned with those of the first layer. Hence, this layer is also of "A" type. The spheres of similarly placed fourth row will be aligned with those of the second row ("B" type). Hence, this arrangement is of ABAB type. In this arrangement, there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two-dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon [Fig. 1.35(b)]. Hence this packing is called two-dimensional hexagonal close packing. It can be seen in Fig. 1.35(b) that in this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards [Fig. 1.35(b)].

c. Close packing in three dimensions

All real structures are three-dimensional structures. They can be obtained by placing two-dimensional layers one above the other. Types of three-dimensional close packing are as below.

i. Three-dimensional close packing from two-dimensional square close-packed layers: The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement, spheres of both the layers are perfectly aligned horizontally as well as vertically as shown in (Fig. 1.36). Similarly, place more layers one above the other. If the arrangement of spheres in the first layer is called "A" type, all the layers have the same arrangement. Thus, this lattice has AAA... type pattern. The lattice thus formed is the simple cubic lattice, and its unit cell is the primitive cubic unit cell (Fig. 1.23).

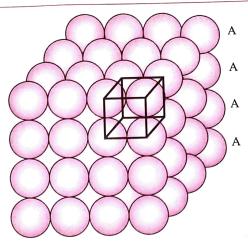
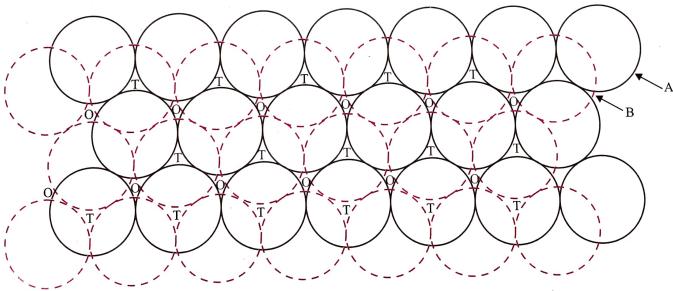


Fig. 1.36 Simple cubic lattice formed by AAA... arrangement

- ii. Three-dimensional close packing from two-dimensional hexagonal close layers: A three-dimensional close-packed structure can be formed by packing layers one over the other.
 - 1. Placing the second layer over the first layer: Take a two-dimensional hexagonal close-packed layer "A" and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer since the spheres of the two layers are aligned differently. It can be observed from Fig. 1.37 that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called tetrahedral voids because a tetrahedron is formed when the centres of these four spheres are joined. They have been marked as "T" in Fig. 1.37. One such void has been shown separately in Fig. 1.38.



s to a related spheres and voids generated in them. T = Tetrahedral void; 0 = Octahedral void

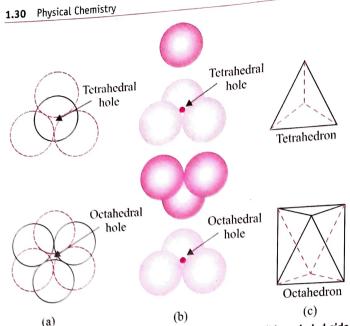


Fig. 1.38 Tetrahedral and octahedral voids: (a) top view, (b) exploded side view, and (c) geometrical shape of the void

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as "O" in Fig. 1.37. Such voids are surrounded by six spheres and are called *octahedral voids*. One such void has been shown separately in Fig. 1.38. The number of these two types of voids depend upon the number of close-packed spheres. Let the number of close-packed spheres be N, then: The number of octahedral voids formed = N

Placing the third layer over the second layer: When third layer is placed over the second, there are two possibilities.

The number of tetrahedral voids formed = 2N

• Covering tetrahedral voids: Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB... pattern. This structure is called hexagonal close-packed (hcp) structure (Figs. 1.39 and 1.40). This type of arrangement of atoms is found in many metals such as magnesium and zinc.

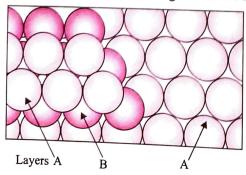
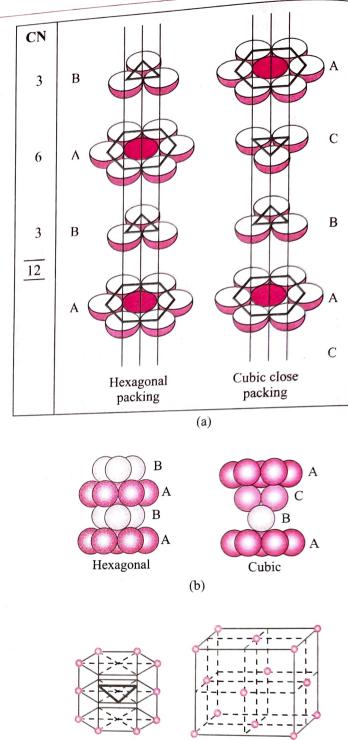


Fig. 1.39 The third layer of spheres lies above the spheres of the first layer to give an AB AB AB... structure (hcp packing)



CN

6

3

12

Fig. 1.40 (a) Hexagonal and cubic close packing exploded view showing stacking of layers of spheres, (b) four layers stacked in each case, and (c) geometry of packing

(c)

Fcc or ccp

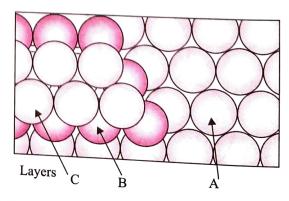


Fig. 1.41 The spheres of the third layer can lie above the depressions in the first layer to give an ABC ABC... arrangement of layers (ccp packing)

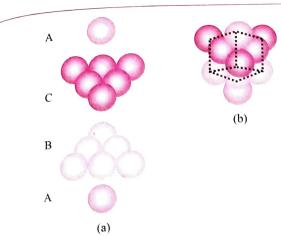


Fig. 1.42 (a) An ABC ABC... arrangement of layers when octahedral void is covered; (b) a fragment of structure formed by this arrangement resulting in a cubic close-packed (ccp) or face- centred cubic (fcc) structure

• Covering octahedral voids: The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called "C" type. Only when the fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs. 1.40 to 1.42. This pattern of layers is often written as ABC ABC ... This structure is called cubic close-packed structure (ccp) or face-centred cubic (fcc) structure. Metals such as copper, silver, and gold crystallize in the structure.

1.14.1 COORDINATE NUMBER (CN) OF HCP AND CCP STRUCTURES

a. CN of an hcp structure: In an hcp structure, each sphere has three nearest neighbours in the plane below (B), six in its own plane (A), and three in the one above (B), having 12 spheres in all at equal distances. Alternatively, this means that the number of nearest neighbours called *coordination number* of each atom in this arrangement of solid is 12 [Fig. 1.43(a)]. It is impossible to pack identical spheres together with a coordination number greater than 12. The close-packed structure adopted by a metal is associated with lowest energy.

In crystals with directional bonds, the coordination number is lower compared to crystals with non-directional bonds (as in the case of metals and ionic compounds).

b. CN of a ccp structure: In a ccp structure, each sphere has three nearest neighbours in the plane below (C), six in its own plane (A), and three in the plane above (B), having 12 spheres in all at equal distances. So CN of ccp structure is also 12 [Fig. 1.43(b)].

So hcp, ccp, or fcc are close-packed structures occupying maximum space (74%) while 26% space remaining vacant. In contrast to this, packing in bcc structure is not that efficient and only 68% is occupied by the atoms.

The voids or holds in crystals are also called *interstices*. Their size acquire importance in relation to the formation of transition metal hydrides, borides, carbides, and nitrides

in which the respective non-metals (H, B, C, and N) are accommodated in the interstices. That is why these compounds are called *interstitial compounds*.

		(a) hcp	(b) ccp	CN
CN		(a) hep		
65	Α		c (2)	
3	В		B () () () () () () () () () (3
6	A		A	6
2	D	(a)	C(b)	3
3 12	В	3 (A May 2)		12

Fig. 1.43 A simplified view of (a) hexagonal closed packing (AB AB ... pattern) and (b) cubic close packing (ABC ABC ... pattern)

Table 1.10 Crystal lattices and coordination numbers of the various types of metallic crystals

Metallic elements	Lattice type	Coordination no.	
Be, Mg, Cd, Zn, Ti	Hexagonal close packing (hcp)	12	
Cu, Ca, Sr, Ag, Au	Cubic close packing (ccp)	12	
Li, Na, K, Rb, Cs	Body-centred cubic arrangement (bcc)	.8	

1.14.2 RELATIONSHIP BETWEEN FORMULA OF A COMPOUND AND NUMBER OF VOIDS FILLED

When particles are close packed resulting in either hcp or ccp structure, two types of voids are formed: tetrahedral voids and octahedral voids

Number of close-packed particles

٠.

- = Number of octahedral voids (OVs)
- = 2 × Number of tetrahedral void (TVs)

Number of effective atoms (Z_{eff}) in ccp and fcc

Packing efficiency in hcp and ccp structures = $\frac{4/\text{unit cell}}{6}\pi$ = 0.74 = 74%

Note: The calculation of packing efficient in ccp is similar to the packing efficiency in fcc [refer section 1.12(c)].

In ionic solids, the bigger ions (usually anions) form the close-packed structures and the smaller ions (usually cations) occupy, the voids. If the cations are small enough then tetrahedral voids are occupied, if bigger, then octahedral voids are occupied. Not all octahedral voids or tetrahedral voids are occupied. In a given

compound, the fraction of octahedral voids or tetrahedral voids that are occupied depends upon the chemical formula of the compound.

1.14.3 STACKING SEQUENCE

It is a sequence in which closest packing can exist.

In stacking sequence, the same layer cannot repeat just after a layer, i.e., A after A is restricted.

If carefully observed, a stacking sequence has fcc, hcp, and combination of fcc and hcp such that all are closely packed with the packing efficiency of 74%.

ILLUSTRATION 1.13

Select the close-packing arrangements in the following:

Sol. (a, b, c)

hcp, ccp, and their combination (hcp + ccp) are close-packed arrangements with packing efficiency of 74%.

1.14.4 LOCATION OF TETRAHEDRAL AND OCTAHEDRAL VOIDS

In a close-packed structure (ccp or fcc), there are both tetrahedral and octahedral voids. If there are N atoms or ions in the close packing, then

Number of $OV_S = N$

Number of TVs = 2N

Location of Tetrahedral Voids

Consider a unit cell of ccp or fcc lattice [Fig. 1.44(a)]. The unit cell is divided into eight small cubes. Each small cube has atoms at alternate corners, i.e., four atoms in all. After joining them, a regular tetrahedron is formed. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total [Fig. 1.44(c)]. Each of the eight small cubes have one void in one unit cell of ccp lattice.

Number to TV = 8/unit cell

 Z_{eff} in ccp or fcc unit cell = 4

Hence, number of TV = 2 \times $Z_{\rm eff}$ in ccp or fcc unit cell. Moreover, in the fcc unit cell, two tetrahedral voids are formed on each of the four nonparallel body diagonals of the cube at a distance of $\sqrt{3}a/4$ from every corner along the body diagonal.

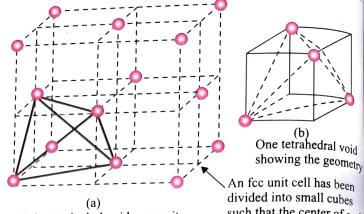
Alternatively, the centres of tetrahedral voids lie 1/4th distance of each body diagonal from one corner or 3/4th distance of each body diagonal from the other corner. [Figs. 1.44(c-e)].

Note: Body diagonal (AB) [Fig. 1.44(e)] = $\sqrt{3}a$

Distance between two tetrahedral voids (A'B') is given as:

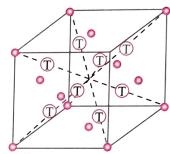
$$\sqrt{3}a = \frac{\sqrt{3}}{4}a + \frac{\sqrt{3}}{4}a + A'B'$$

$$\Rightarrow A'B' = \frac{1}{2} \times \sqrt{3} a = \frac{1}{2} \times \text{Body diagonal}$$

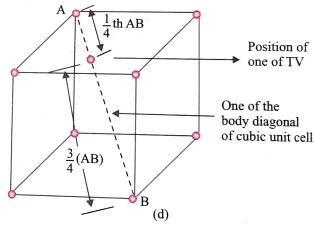


Eight tetrahedral voids per unit cell of ccp structure

An fcc unit cell has been divided into small cubes such that the center of each sub-cube is the location of tetrahedral void



(c) Location of all the 8 tetrahedral voids



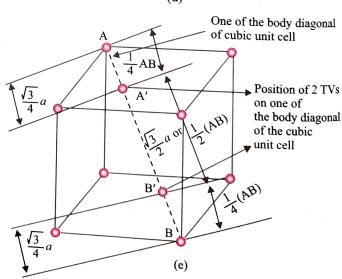


Fig. 1.44

Nearest distance between 2 TV's = $\frac{\sqrt{3}}{2}a$

Location of Octahedral Voids

Consider again a unit cell of ccp or fcc lattice [Fig. 1.45(a)]. The body centre of the cube C is not occupied but it is surrounded by six atoms on face centres [marked in Fig. 1.45(a) as 1 to 6]. On joining these face centres, an octahedron void is formed.

Thus, number of OV at the body centre of the cube = 1

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges [Fig. 1.45(b)]. It is surrounded by six atoms, three belonging to the same unit cell (two on the corners and one on face centre), and three belonging to two adjacent unit cells.

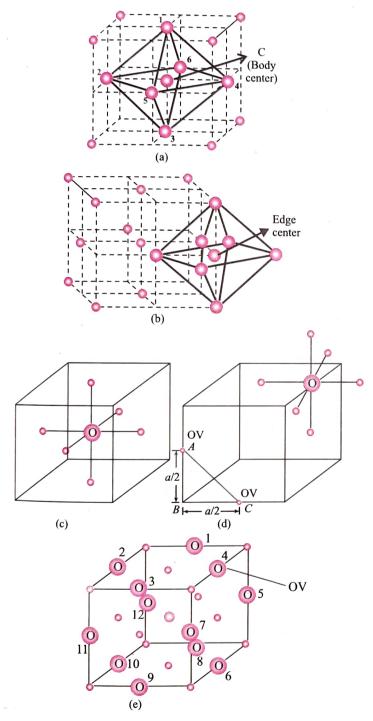


Fig. 1.45 Location of octahedral voids per unit cell of ccp or fcc lattice
(a) at the body centre of the cube, (b) at the centre of each edge (only
one such voids is shown), (c) octahedral void at the body centre (share by
none), (d) octahedral void at the edge centre (shared by four unit cells),
and (e) 12 octahedral voids at the edge centres

Nearest distance between 2 OV's [Fig. 1.45(d)]

$$(AC)^2 = (AB)^2 + (BC)^2 = \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 = \frac{a^2}{2} : AC = \frac{a}{\sqrt{2}}$$

Since each edge of the cube is shared between four adjacent unit cells, so only 1/4th of each void belongs to a particular unit cell [Figs. 1.45(c-e)].

 \therefore OV at the body centre of the cube = 1

OV at the 12 edges of the cube and shared between four unit cells = $12 \times \frac{1}{4} = 3$

 \therefore Total number of OVs = 1 + 3 = 4

 $Z_{\rm eff}$ in ccp or fcc structure = 4

 \therefore Number of OVs = Z_{eff} in ccp or fcc unit cell

ILLUSTRATION 1.14

A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make ccp and those of element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Sol. The ccp lattice is formed by the element Y.

First method

 $\therefore Z_{\text{eff}} \text{ of Y (as anions)} = 4$

Number of TVs = 8/unit cell

Number of OVs = 4/unit cell

Since all the OVs are occupied by X.

 \therefore Number of X (as cations) = 4.

 $\therefore Formula = X_4Y_4 = 4XY$

Second method

Let Z_{eff} of Y (as anions) = 1

Number of TVs = 2/atom or anion

Number of $OV_S = 1/atom$ or anion.

Since all the OVs are occupied by X.

- \therefore Number of X (as cations) = 1
- \therefore Formula = XY

ILLUSTRATION 1.15

Atoms of element B form hcp lattice and those of element A occupy two-thirds of tetrahedral voids. What is the formula of the compound formed by elements A and B?

Sol. The hcp lattice is formed by element B.

First method

 $\therefore Z_{\text{eff}}$ of B (hcp lattice) = 6

Number of TV = 12/unit cell

Number of OV = 6/unit cell

Since element A occupies two-thirds of TVs

$$\therefore$$
 Number of A = $\frac{2}{3} \times 12 = 8$

$$\therefore$$
 Formula = $A_8B_6 = A_4B_3$

Second method

Let Z_{eff} of B = 1

Number of TV = 2/atom

Number of OV = 1/atom

$$\therefore \text{ Number of } A = \frac{2}{3} \times TV = \frac{2}{3} \times 2 = \frac{4}{3}$$

 \therefore Formula = $A_{4/3}B_1$

Simplifying: A₄B₃

ILLUSTRATION 1.16

An element has a bcc structure with a cell edge of 288 pm. The density of the element is 7.2 g cm⁻³. How many atoms are present in 208 g of the element?

Sol. Volume of unit cell =
$$(288 \text{ pm})^3 = (288 \times 10^{-12} \text{ m})^3$$

= $(288 \times 10^{-10} \text{ cm})^3$
= $2.39 \times 10^{-23} \text{ cm}^3$

For bcc,
$$Z_{\text{eff}} = 2$$

$$\therefore \rho = \frac{Z_{\text{eff}} \times Aw}{N_{\text{A}} \times a^3}$$

7.2 g cm⁻³ =
$$\frac{2 \times Aw}{6 \times 10^{23} \times 2.39 \times 10^{-23} \text{ cm}^3}$$

$$\therefore Aw/2 = 7.2 \times 6 \times 10^{23} \times 2.39 \times 10^{-23} \text{ g}$$

$$\therefore Aw = 7.2 \times 3 \times 2.39 \text{ g}$$

$$\therefore$$
 7.2 × 3 × 2.39 g of element contains = N_A atoms

$$= 6 \times 10^{23}$$
 atoms.

$$\therefore 208 \text{ g of the element contains} = \frac{6 \times 10^{23} \times 208}{7.2 \times 3 \times 2.39}$$
$$= 24.16 \times 10^{23} \text{ atoms}$$

Alternatively

Volume of 208 g of the element =
$$\frac{\text{Mass}}{\text{Density}} = \frac{208 \text{ g}}{7.2 \text{ g cm}^{-3}}$$

= 28.88 cm³

Number of unit cells in this volume

$$= \frac{28.88 \,\text{cm}^3}{2.39 \times 10^{23} \,\text{cm}^3/\text{unit cell}}$$

$$= 12.08 \times 10^{23}$$
 unit cells

Since each bcc cubic unit cell contains 2 atoms, therefore the total number of atoms in 208 g

= 2 (atoms/unit cell)
$$\times$$
 12.08 \times 10²³ unit cells

$$= 24.16 \times 10^{23} \text{ atoms}$$

ILLUSTRATION 1.17

X-ray diffraction studies show that copper crystallizes in an fcc unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g cm³. Calculate the atomic mass of copper.

Sol. In case of fcc lattice, number of atoms per unit cell, Z = 4 atoms

$$\therefore Aw = \frac{\rho N_{\rm A}a^3}{Z_{\rm eff}}$$

$$= \frac{8.92 \text{ g cm}^3 \times 6.022 \times 10^{23} \text{ atoms mol}^{-1}}{4 \text{ atoms}}$$

 $= 63.1 \text{ g mol}^{-1}$

Atomic mass of copper = 63.1μ

ILLUSTRATION 1.18

Silver forms ccp lattice and X-ray studies of its crystals sh_{0} that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (atomic mass = 107.9 u).

Sol. Since, the lattice is ccp, the number of silver atoms punit cell = Z = 4

Atomic mass of silver = 107.9 g mol^{-1}

$$= 107.9 \times 10^{-3} \text{ kg mol}^{-1}$$

Edge length of unit cell = $a = 408.6 \text{ pm} = 408.6 \times 10^{-12}$

Density, (
$$\rho$$
) = $\frac{Z_{\text{eff}} \times Aw}{a^3 \times N_A}$
= $\frac{4 \times (107.9 \times 10^{-3} \text{ kg mol}^{-1})}{(408.6 \times 10^{-12} \text{ m})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}$
= $10.5 \times 10^3 \text{ kg m}^{-3} = 10.5 \text{ g cm}^{-3}$

ILLUSTRATION 1.19

Metallic gold crystallizes in the fcc lattice. The length of the cubic unit cell is a = 4.242 Å.

- a. What is the closest distance between gold atoms?
- **b.** How many "nearest neighbours" does each gold atom have at the distance calculated in (a)?
- c. What is the density of gold? (Aw of $Au = 197.0 \text{ g mol}^{-1}$

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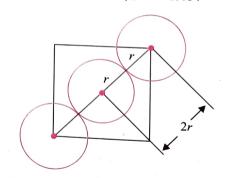
d. Prove that the packing factor for gold is 0.74.

Sol. In fcc,
$$Z_{\text{eff}} = 4$$
.

For fcc, atomic radius
$$(r) = \frac{a}{2\sqrt{2}}$$

a. Closest distance between two Au atoms = 2r

$$= 2 \times \frac{a}{2\sqrt{2}} = \frac{a}{\sqrt{2}} = \frac{4.242}{\sqrt{2}} = \frac{4.242}{1.414} = 3.0 \text{ Å}$$



b. As the coordination number of fcc = 12.

So there are 12 nearest neighbours in all, the number expected for a close-packed structure.

c. Density =
$$\rho = \frac{Z_{\text{eff}} \times Aw}{N_A \times a^3}$$

= $\frac{4 \times 197 \text{ g}}{6 \times 10^{23} \times (3.0 \times 10^{-8} \text{ cm})^3}$
= 48.64 g cm^{-3}

d. Packing factor for fcc lattice = $\frac{\sqrt{2}}{6}\pi = 0.7404$ [For proof refer to section 1.12(c)]

ILLUSTRATION 1.20

If the radius of an atom of an element is 75 pm and the lattice type is body-centred cubic, what is the edge length of the unit cell?

Sol. For BCC,
$$r = \frac{\sqrt{3}}{4}a$$

or $a = \frac{4r}{\sqrt{3}} = \frac{4 \times 75}{1.732} = 173.2 \text{ pm}$

ILLUSTRATION 1.21

The radius of an atom of an element is 500 pm. If it crystallizes as a face-centred cubic lattice, what is the length of the side of the unit cell?

Sol. For fcc,
$$r = \frac{a}{2\sqrt{2}}$$

or $a = 2\sqrt{2}$ $r = 2 \times 1.414 \times 500$ pm = 1414 pm

ILLUSTRATION 1.22

Sodium has a bcc structure with nearest neighbour distance of 365.9 pm. Calculate its density. (Atomic mass of sodium = 23)

Sol. For the bcc structure, nearest neighbour distance (d) is related to the edge (a) as

$$d = \frac{\sqrt{3}}{2} a$$
or $a = \frac{2}{\sqrt{3}} d = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$

For bcc structure, $Z_{\text{eff}} = 2$

For sodium, Aw = 23

$$\therefore r = \frac{Z_{\text{eff}} \times Aw}{a^3 \times N_{\text{A}} \times 10^{-30}}$$

$$= \frac{2 \times 23}{(422.5)^3 \times (6.02 \times 10^{23}) \times 10^{-30}} \text{ g cm}^{-3} = 1.51 \text{ g cm}^{-3}$$

ILLUSTRATION 1.23

A face-centred cubic element (atomic mass 60) has a cell edge of 400 pm. What is its density?

Sol. For the face-centred cubic,
$$Z_{\text{eff}} = 4$$

$$\rho = \frac{Z_{\text{eff}} \times Aw}{a^3 \times N_{\text{A}} \times 10^{-30}} \text{ g cm}^{-3}$$

$$= \frac{4 \times 60}{(400)^3 \times (6.02 \times 10^{23}) \times 10^{-30}} = 6.23 \text{ g cm}^{-3}$$

ILLUSTRATION 1.24

Xenon crystallizes in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

Sol. Here
$$a = 620$$
 pm, $d = ?$, $r = ?$

For the face-centred cubic lattice,

$$d = \frac{a}{\sqrt{2}} = \frac{620 \text{ pm}}{1.414} = 438.5 \text{ pm}$$

$$r = d/2 = 438.5/2 = 219.25 \text{ pm}$$

1.15 STRUCTURE OF IONIC CRYSTALS

In ionic crystals, there are two types of ions, cations and anions. Both have different sizes and charges. Due to the attraction between opposite charges, there is a tendency of one type of charge to surround ions of the opposite charge. Due to difference in ionic sizes, the structure of a given solid is determined by geometrical considerations during the packing of ions of different sizes.

The cation is assumed to be the smaller ion. The number of anions surrounding a central cation is called the *coordination* number or ligancy. The ligancy is a function of the sizes of the ions. The ionic radius ratios of cation (r_c) and anion (r_a) is very important in the determination of the crystal structures of an ionic substance.

If anions are arranged around a cation and vice versa and keeping the size of the cation same, as the size of the anion decreases, the ligancy (or coordination number) increases (Fig. 1.46).

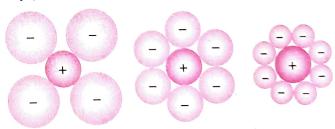


Fig. 1.46 Illustration of the importance of ionic ratio in packing (as the ratio r_c/r_a increases more number of anions can be arranged around cations)

1.15.1 RADIUS RATIO RULES

Following conditions must be satisfied simultaneously during the stacking of ions of different sizes in an ionic crystal:

- **a.** An anion and a cation are assumed to be hard spheres always touching each other.
- **b.** Anions generally will not touch but may be close enough to be in contact with one another in a limiting situation.
- c. A cation should surround itself with as many anions as possible. Each ion tends to surround itself with as many ions of opposite sign as possible to reduce the potential energy. This tendency promotes the formation of close-packed structures.

When a cation is very small compared to an anion, it is easily seen that only two anions can be neighbours to the cation in order to satisfy all the above three conditions. Consider the configuration as shown in Fig. 1.47(a) below. Here, the three surrounding anions are touching one another as well as the central cation.

$$r_c/r_a = 0.155$$
 $0 < r_c/r_a < 0.155$ $0.155 < r_c/r_a \le 0.225$ (a) $0 < r_c/r_a < 0.155$ (c)

Fig. 1.47 Triangular coordination of anions around a central cation: (a) critical configuration, (b) unstable configuration, and (c) stable (but not critical) configuration

The ratio of the cation to anion radius r_c/r_a for this configuration is 0.155, which can be worked out from the simple geometry (see Fig. 1.48). The triangular arrangement in (a) is one of the limiting situations. The radius ratio is said to be a critical value because for the value of r_c/r_a smaller than 0.155, the central cation will rattle in the hole and not touch all the three anions at the same time, as illustrated in (b). This violates condition (a) above and leads to instability. When the radius ratio is less than 0.155, then the on way to satisfy all three conditions is to reduce the number of anio to 2. For values of r_c/r_a slightly greater than 0.155, all the anim touch the central cation but do not touch one another, as shown (c). All three conditions of stability are still satisfied. This situaling will prevail till the radius ratio increases to 0.225, the next high critical value corresponding to a tetrahedral (four) coordination $r_c/r_a = 0.225$, the four surrounding anions touch one another and also the central cation. This configuration is same as that obtain by fitting the largest possible sphere in the tetrahedral void of close-packed structure (see Fig. 1.49).

A ligancy of 5 does not satisfy all the three conditions for stable configuration because it is always possible to have six anions as an alternative to any arrangement that contain five anions, without a change in the radius ratio. The critical condition for octaheral (six) coordination occurs at r/r0.414, which is same as the size of the octahedral void in a close packed structure. Ligancies of 7, 9, 10, and 11 are again no permissible.

The radius ratio ranges in which different values of ligancy at obtained are summarized in Table 1.11. At the end of the table the limiting case of $r_c/r_a = 1$ is identified with configurations close packing of equal-sized spheres.

Table 1.11 Ligancy as a function of radius ratio in 1:1 or AB-type structure

S. No.	Ligancy or coordination number	Range of radius ratio $(r \oplus /r \ominus)$	Configuration	Structure type	Examples
1.	2	$0.0 < \frac{r^*}{R} < 0.155$	Linear		_
2.	3	$0.155 \le \frac{r}{R} < 0.225$	Triangular		<u> </u>
3.	4	$0.225 \le \frac{r}{R} < 0.414$	Tetrahedral	ZnS	CuCl, CuBr, CuI, BaS, HgS
4.	6 .	$0.414 \le \frac{r}{R} < 0.732$	Octahedral	NaCl	MgO, NaBr, CaS, MnO, KBr, Ca
5.	8	$0.732 \le \frac{r}{R} < 1.0$	Cubic	CsCl	CsI, CsBr, TlBr, NH ₄ Br
6.	12	$\frac{r}{R} = 1.0$	fcc or hcp		•
*r = rac	dius of cation; R = radiu.		F		-

cation; R = radius of anion

Note: There are exceptions for each type of structure, e.g., BeS $(r_c/r_a = 0.19)$ has ZnS (sphalerite) type structures; LiI $(r_c/r_a = 0.34)$, LiBr $(r_c/r_a = 0.38)$, KCl $(r_c/r_a = 0.77)$, RbCl $(r_c/r_a = 0.83)$, BaO $(r_c/r_a = 0.97)$ have NaCl-type or rock salt

Critical Radius Ratio for Triangular Coordination

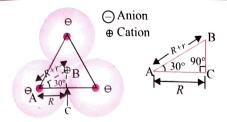
The critical condition for triangular coordination is shown in Figure 1.56. The three anions touch one another as well as the central cation. From the simple geometry, we can write:

$$\cos 30^{\circ} = \frac{\text{Base}}{\text{Hypotenuse}} = R/R + r$$

$$(R + r) \cos 30^{\circ} = R$$

$$\Rightarrow R + r = \frac{2}{\sqrt{3}} R \ (\because \cos 30^{\circ} = \sqrt{3}/2)$$

$$\Rightarrow \frac{r}{R} = \frac{2}{\sqrt{3}} - 1 = 0.155$$



R =Radius of anion r =Radius of cation

Fig. 1.48

Critical Radius Ratio for Tetrahedral Coordination or Relation Between Radius (r) of the TV and Radius (R) of the Atoms in Close-Packed Structures

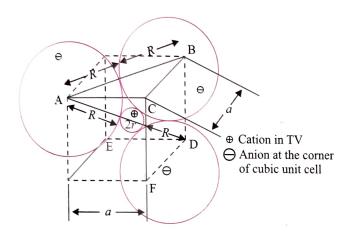


Fig. 1.49

The anions touch each other as well as the central cation. Let r is the radius of TV (cation), R is the radius of anions, and a is the edge length of the cubic unit cell.

From the right-angled triangle ABC, face diagonal (AB) is

$$AB = \sqrt{(AC)^2 + (BC)^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

Since anions at A and B are actually touching each other in the close packing, face diagonal (AB) = 2R.

Hence,
$$2R = \sqrt{2}a$$
 or $R = \frac{1}{\sqrt{2}}a$...(i)

Again from the right-angled triangle ABD,

Body diagonal (AD) =
$$\sqrt{(AB)^2 + (BD)^2}$$

= $\sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$

$$\therefore AD = 2(R + r) = \sqrt{3} a$$

Hence,
$$(R + r) = \frac{\sqrt{3}}{2} a$$
 ...(ii)

Dividing Eq. (ii) by Eq. (i), we get

$$\frac{(R+r)}{R} = \frac{\sqrt{3}a/2}{a/\sqrt{2}} = \frac{\sqrt{3}}{\sqrt{2}}$$

or
$$1 + \frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

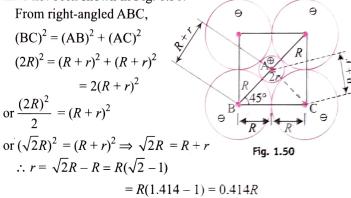
or
$$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1$$

$$= \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.732 - 1.414}{1.414} = 0.225$$
or $r = 0.225R$

$$\begin{pmatrix} \text{Radius of TV} \\ \text{i.e., cation} \end{pmatrix} = \begin{pmatrix} 0.225 \text{ radius} \\ \text{of the anion} \end{pmatrix}$$
or $r_c = 0.225r_a$

Critical Radius Ratio for Octahedral Coordination or Relation Between Radius (r) of the OV and Radius (R) of the Atoms in Close-Packed Structures

The anions touch one another as well as the central cation present in OV. A sphere above and a sphere below this small cation (sphere) have not been shown in Fig. 1.50.



$$\therefore$$
 Radius (r) of OV = 0.414R

Alternatively

$$(2r+2R)\cos 45^\circ = 2R \Rightarrow r/R = \sqrt{2}-1 = 0.414$$

In case of ionic compounds, anions are usually present in close packing and cations occupy the voids, we can also write

- **a.** For cations occupying TVs, $r_c = 0.225r_a$.
- **b.** For cations occupying OVs, $r_c = 0.414r_a$.

Hence, a TV is much smaller than the OV. Moreover, the maximum size of the cation occupying the void is 0.414*R*. If the smaller spheres (i.e., cation) to occupy the voids have size larger than this, the arrangement will no longer be close packed.

Critical Radius Ratio for Body-Centred Co-ordination or Relation Between Radius (r) of the Body-Centred Void and Radius (R) of the Atoms

The critical condition for cubic void is shown in Fig. 1.51. The anions touch one another (as in sc) as well as the central cation. From the simple geometry, we can write

$$a = 2R$$
 and $\sqrt{3} a = 2R + 2r$

$$\Rightarrow \frac{r}{R} = \sqrt{3} - 1 = 0.732 \Rightarrow r = 0.732R$$

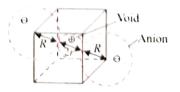


Fig. 1.51

1.15.2 COORDINATION NUMBER IN SOME IONIC COMPOUNDS

The ligancy rules outlined above are obeyed in a number of cases. For example, in the NaCl crystal, the ratio $r_{\rm Na} \oplus / r_{\rm Cl^{()}} = 0.54$, which lies between 0.414 and 0.732. As listed in Table 1.11, the predicted ligancy is 6. The octahedral geometry of six chlorine ions surrounding a central cation is experimentally observed. In MgO, $r_{\rm Mg^{2+}}/r_{\rm O^{2-}}$ = 0.59 and again the octahedral coordination is observed. In CsCl. $r_{Cs} \oplus r_{Cl} = 0.73$, it is difficult to predict whether a six-fold or an eight-fold coordination will occur. It so turns out that the eight-fold coordination is observed. In this case, that is, every cesium cation is surrounded by eight chlorine anions.

The Si-O bond in silica as well as in silicates is about 50% ionic and 50% covalent. Here, the central silicon cation is surrounded by four oxygen anions located at the corners of a regular tetrahedron. This arrangement satisfies both the ligancy rules (as $r_c/r_a = 0.29$, the tetrahedral coordination is predicted from Table 1.11, as well as the orientation relationships of sp^3 bonds).

The stability criteria listed above for predicting the ligancy may not always be valid. If the directional characteristics of bonding persist to any significant degree, the considerations based on the radius ratio alone will not lead to the correct prediction of ligancy. In the above-discussed example of Si-O coordination, the radius ratio criterion and the bond angle requirement happen to coincide. In ZnS, where the bond is more covalent than ionic, the ligancy predicted from $r_{Z_n^{2+}}/r_{S^{2-}} = 0.48$ is octahedral. Yet the four-fold coordination characteristic of (sp^3) bonding is observed.

In the formation of ionic crystals, the ligancy rules described above determine the local packing around a cation. The long-range arrangement of ions in the crystal is dependent on the following factors:

- a. In the crystal, the overall electrical neutrality should be maintained, whatever be the net charge on a local group of a cation and surrounding anions. For example, in NaCl, where a cation is surrounded by six anions, the net charge on NaCl₆ is 5. Evidently, this has to be neutralized in the long-range arrangement.
- b. The ionic bond being non-directional, the ions are packed as closely as possible in the crystal, consistent with the local coordination.

When the cation charge is not more than 2 or at best 3 and when the radius ratio is in the range 0.414-0.732, the crystal structure can be described as fcc or hcp packing of anions with the cations occupying all or part of octahedral voids in the structure. The fraction of octahedral voids that are filled depends on the number of cations to anions in the chemical formula. Thus, for the rock salt (NaCl) structure, adopted by hundreds of binary ionic compounds, $r_{\rm Na\oplus}$ / $r_{\rm Cl^{\odot}}$ = 0.54 and the anion packing is fcc with all octahedral voids filled with sodium cations. Note that there is one octahedral void per sphere in a close-packed array. A unit cell of NaCl crystal is shown in Fig. 1.52, with the larger chlorine ions occupying the corner and face-centred cubic positions and the sodium ions in the octahedral voids. The octahedral positions are at the body centre and at the

midpoints of the cube edges. Note that unlike in the monoatomie fcc crystal, the chlorine ions do not touch one another along the face diagonal. This is so because the radius ratio of 0.54 is greaten than the size of the octahedral void in a close-packed structure which is 0.414. The fcc close packing is "opened up" here to the extent necessary to accommodate the sodium cations in the octahedral voids.

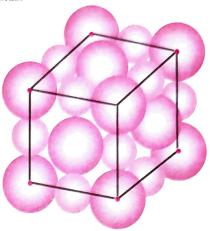


Fig. 1.52 A unit cell of NaCl with Cl^{\odot} at fcc positions and Na[⊕] ions in the octahedral voids

As the fcc positions and octahedral void centres are interchangeable like the body centre and body corners in the bcc cell, the NaCl structure can also be described as two interpenetrating monoatomic fcc cells, one corresponding to the anions and the other to the cations. The basis of the NaCl structure is one sodium ion plus one chlorine ion. The sum of their radii $r_{\text{Na}} + r_{\text{Cl}} = a/2$, where a is the lattice parameter.

When r_c / r_a is in the range of 0.7312 to 1, an eight-fold coordination is observed. CsCl with $r_{\rm Cs} \oplus /r_{\rm Cl} = 0.91$ is a typical example of this structure. The cesium ions are at the body centre and the chlorine ions are at body corners. The space lattice is simple cubic, with a basis of one cesium ion plus one chlorine ion per lattice point.

1.16 STRUCTURES OF SIMPLE IONIC COMPOUNDS

Simple ionic compounds are the compounds of the type AB or AB where A and B represent the positively and negatively charged ions, respectively. It is more difficult to describe the structures of even these simple ionic compounds as compared to those of the elements. This is because an element consists of only one type of atoms, all of which occupy the lattice points, e.g., in case of copper which is face-centred cubic (fcc), all lattice points are occupied by copper atoms. On the other hand, in case of ever simple ionic compounds, the arrangement of both A and B ion has to be described, as given below.

1.16.1 SIMPLE IONIC COMPOUNDS OF TYPE AB

Ionic compounds of the type AB means compounds having positively and negatively charged ions in the ratio 1:1. Thes compounds have any one of the following three types of structures

- a. Rock salt (NaCl) type structure
- b. Caesium chloride (CsCl) type structure
- c. Zinc blende (ZnS) or sphalerite type structure

The main features of each of these structures are discussed below.

Rock Salt (NaCl) Type Structure

The structure of NaCl is as shown in Fig. 1.53. The main features of this structure are as follows:

a. It has a face-centred cubic (fcc) arrangement (also called cubic close packing, i.e., ccp) in which Cl[©] ions occupy the corners and face centres of the cube while Na[©] ions are present at the body centre and edge centres.

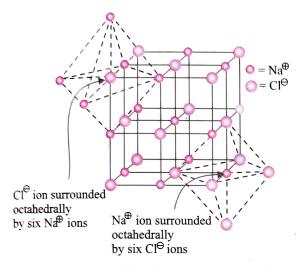


Fig. 1.53 NaCl structure

- b. Each Na^\oplus ion is surrounded by six Cl^\ominus ions and each Cl^\ominus ion is surrounded by six Na^\oplus ions. In other words, the Na^\oplus ions as well as Cl^\ominus ions have coordination number of 6, i.e., this structure has 6: 6 coordination (i.e., Cl^\ominus ions being larger in size are present in the close packing while Na^\oplus ions are present in all the octahedral voids. Further, for exact fitting of cations and anions, the radius ratio r_\oplus/r_\ominus should be 0.414. The actual value of $r_{\mathrm{Na}^\oplus/\mathrm{Cl}^\ominus}=0.525$. Hence, to accommodate large Na^\oplus ions, Cl^\ominus ions move apart slightly, i.e., they do not touch each other. Hence, it forms an expanded face-centred lattice).
- c. A unit cell of NaCl consists of four NaCl units, i.e., four Na $^{\oplus}$ ions and four Cl $^{\ominus}$ ions as calculated below. Eight Cl $^{\ominus}$ ions are present on the corners and six Cl $^{\ominus}$ ions on the faces so that Cl $^{\ominus}$ ions per unit cell = $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$. Similarly, 12 Na $^{\oplus}$ ions are present on the edges and one within the body so that Na $^{\oplus}$ ion per unit cell = $\frac{1}{4} \times 12 + 1 = 4$.

A few examples of the compounds having structure similar to that of NaCl are as follows:

- a. Halides of alkali metals (except those of cesium) and that of ammonium
- b. Oxides and sulphides of alkaline earth metals (except BeS)
- c. Halides of silver (except silver iodide)

Caesium Chloride (CsCl) Type Structure

The structure of CsCl is as shown in Figs. 1.54(a) and 1.54(b).

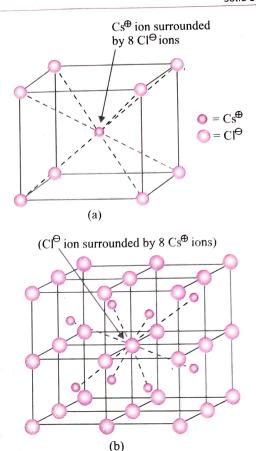


Fig. 1.54 (a) A unit cell of CsCl structure; and (b) the concept of reversibility in the case of CsCl crystal such that Cl[⊖] lies in the simple cubic of Cs[⊕]

The main features of this structure are as follows:

- a. It has body-centred cubic (bcc) arrangement.
- Each Cs[⊕] ion is surrounded by eight Cl[⊕] ions and each Cl[⊕] ion is surrounded by eight Cs[⊕] ions, i.e., this structure has 8:8 coordination.
- c. A unit cell of CsCl consists of only one unit of CsCl, i.e., one Cs^{\oplus} ion and one Cl^{\ominus} ion (because each ion present at the corner is shared by eight unit cells) [The ratio $r_{\text{Cs}}_{\oplus}/r_{\text{Cl}}_{\ominus} = 0.93$ which is greater than expected for exact fitting (0.732)].

A few examples of compounds having CsCl structure are: CsBr, CsI, CsCN, TlCl, TlBr, TlI, and TlCN.

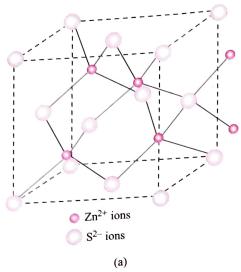
Zinc Blende (ZnS) Type Structure

The structure of ZnS is as shown in Fig. 1.55(a). It exits in two different forms, zinc blende and wurtzite. Both are 4:4 structures. The main features of this structure are as follows:

- **a.** The arrangement as possessed by ZnS is called cubic close packing (ccp) in which S²⁻ ions are present at the corners as well as at the centre of each face of the cube.
- **b.** Each Zn^{2+} ion is surrounded tetrahedrally by four S^{2-} ions and each S^{2-} ion is surrounded tetrahedrally by four Zn^{2+} ions. Thus, this structure has 4 : 4 coordination. (The ratio $r_{Zn^{2+}}/r_{S^{2-}} = 0.40$ which is greater than expected for exact fitting (0.225).)

Note: Zn²⁺ ions are present in alternate tetrahedral voids.

In an fcc unit cell, there are 8 TVs. Thus, there are four Zn²⁺ ions and 4 S²⁻ ions giving 4 ZnS units per unit cell.



Here electronegativity difference between Zn and S is very small (EN for Zn = 1.6 and EN for S = 2.5). Therefore, the bond between Zn and S has significant covalent character.

Figure 1.55(b) gives the structure of diamond and it is found that it is similar to that of ZnS (sphalerite).

A few examples of ionic compounds having ZnS structures are: CuCl, CuBr, CuI, AgI, and BeS.

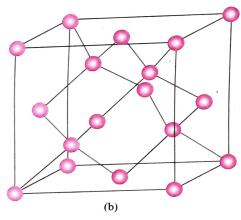


Fig. 1.55 (a) Structure of Zns. (b) Diamond structure. Both structures (a) and (b) are identical

1.16.2 SIMPLE IONIC COMPOUNDS OF TYPE AB₂ (FLUORITE TYPE)

The next simplest type of ionic crystal structure is the 1:2 type popularly known as AB₂-type structure. Calcium fluoride (fluorite), CaF2, is an example of AB2-type compounds (Fig. 1.56). Other ionic structures similar to CaF₂ structure are grouped under fluorite structure. The calcium ions, Ca2+, are located at the face-centred cubic lattice points and, therefore, have cubic close-packed arrangement. The fluoride ions (F^{\odot} ions) occupy all the 8 tetrahedral voids. Thus, there are 4 Ca²⁺ ions and 8 F[©] ions in the unit cell of calcium fluoride.

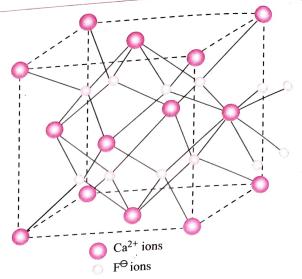


Fig. 1.56 Structure of CaF₂ (fluorite)

Note: Here negative ions (anions) (F[©] ions) are present in a tetrahedral voids.

Coordinate number of AB₂-type structure Since each Ca⁺² surrounded by = 8 F^{\odot} ions Each F^{\odot} is surrounded by = 4 Ca^{+2} ions

Thus, the structure has 8: 4 coordination. Other ionic compound that have fluoride structure are SrF₂, BaF₂, PbF₂, and BaCl₂.

1.16.3 SIMPLE IONIC COMPOUNDS OF TYPE A₂B (ANTIFLUORITE TYPE)

Several A2B-type or 2:1-type compounds have structures opposit to the fluorite structure; hence the so-called antifluorite structure In an antifluorite structure the position of cations and anions a obtained in the fluorite structure gets reversed. In this structure the smaller cations occupy the positions of fluoride ions and the larger anions occupy the positions of the calcium ions in the fluoring structure. For example, in Na2O, oxide ions (O2-) have a cubit close-packed arrangement and Na[®] ions occupy all the tetrahedra voids (Fig. 1.57). There are several oxides and sulphides which have antifluorite structure such as Li₂O, K₂O, Rb₂O, and Rb₂S.

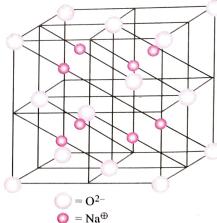


Fig. 1.57 Na₂0 structure of antifluorite type

Coordination number of A₂B-type structure: Each O²⁻ ions is surrounded by eight Na[⊕] ions. Each Na[⊕] ion is surrounded by four O²⁻. Thus, the structure has 4: 8 coordination.

1.16.4 RELATION BETWEEN EDGE LENGTH A AND RADIUS OF CATION AND ANION IN IONIC COMPOUNDS

a. For bcc-type (CsCl) structure

In CsCl lattice, anions (e.g., Cl[©] ions) are at corners of the cube and cations (e.g., Cs[®] ions) are at the body centre of the cube as shown in Fig. 1.58.

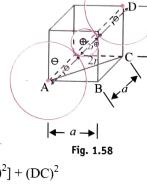
From the figure, it is clear that AD is the body diagonal of the cube.

$$\therefore (AD)^{2} = (AC)^{2} + (DC)^{2}$$

$$= [(AB)^{2} + (BC)^{2}] + (DC)^{2}$$

$$(2r_{\odot} + 2r_{\oplus})^{2} = 3a^{2}$$

$$\therefore (r_{\oplus} + r_{\odot}) = \frac{\sqrt{3}}{2}a$$



b. For fcc-type (close-packed) structures (e.g., NaCl type)

In NaCl lattice, anions (i.e., Cl^{\odot} ions) are at the corners and face centre of the cube. Thus, $Z_{\rm eff}$ of $Cl^{\odot} = 4$.

Cations (i.e., Na^{\oplus} ions) are in all octahedral voids formed at the edge centre and body centre of the cube as shown in Fig. 1.59:

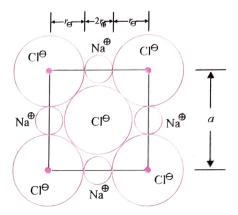


Fig. 1.59

From the figure, it is clear

$$(2r_{\oplus} + 2r_{\odot}) = a$$

$$\therefore (r_{\oplus} + r_{\odot}) = \frac{a}{2}$$

Table 1.12 Summary of the main characteristics and examples of some simple ionic solids

Crystal structure	Brief description	Examples	Coordination number	Number of formula unit/units cell	Coordination
Type AB: Rock salt (NaCl) type Radius:	It has fcc arrangement in which $C1^{\odot}$ ion occupy the corners and face centres of a cube while Na^{\oplus} ions are present at the body and edge centres. $(r_{\oplus} + r_{\odot}) = a/2$	Halides of Li, Rb AgF, AgBr, NH ₄ C1, NH ₄ Br, NH ₄ I	Each Na [®] is surrounded by 6 Cl [®] . Each Cl [®] is surrounded by 6 Na [®] Na [®] occupy all OVs. & all TV are empty.	General formula $A_4B_4 \text{ or } 4AB$ $Z_{\text{eff}} = 4$	6:6
Caesium chloride (CsCl) type	It has bcc arrangement with Cs [⊕] at the body centre and Cl [⊙] ions at the corners of a cube or vice versa.	CsCl, CsBr, Csl, CsCN, TlCl, TlBr	Each Cs [®] is surrounded by 8 Cl [©] . Each Cl [©] is sur-	General formula AB	8:8
Radius for bcc type	$(r_{\oplus} + r_{\ominus}) = \frac{\sqrt{3}}{2}a$	TII, and TICN	rounded by 8 Cs [⊕] .	$Z_{\text{eff}} = 1$	
Zinc olende (ZnS) sphalerite) ype	It has ccp arrangement in which S^{2-} ions form fcc and each Zn^{2+} ion is surrounded tetrahedrally by S^{2-} ion and vice versa.	CuCl, CuBr, Cul, AgI 50% of TV are empty 100% of OV are empty	Each Zn ²⁺ is surrounded by 4 S ²⁻ . Each S ²⁻ is surrounded by 4 Zn ²⁺ . Zn ⁺² are in alternate TVs.	General formula $A_4B_4 \text{ or } 4AB$ $Z_{\text{eff}} = 4$	4:4
Type AB ₂ Cluorite CaF ₂) type	It has ccp arrangement in which Ca^{2^+} ions form fcc with each Ca^{2^+} ion surrounded by $8~F^{\odot}$ ions and each F^{\odot} ion by $4~Ca^{2^+}$ ions	BaF ₂ , BaCl ₂ , SrF ₂ , SrCl ₂ , CdF ₂ , PbF ₂	Each Ca ⁺² is surrounded by 8 F ^O . Each F ^O is surrounded by 4 Ca ²⁺ . F ^O ions occupy all the 8 TVs.	General formula A_4B_8 or AB_2 $Z_{eff} = 4$ 100% TV occupied 100% OV empty.	8:4

Anti-

fluorite type

1.17 STRUCTURE OF DIAMOND

Solids which follow the structure of diamond are called "diamond cubic" [Fig. 1.55(b)]. Diamond has fee structure with four more atoms that are found to be present in the alternate tetrahedral voids.

So. \mathbb{Z}_{eff} of C-atoms in diamond cubic = Z_{eff} in fee unit cell + Z_{eff} in alternate TVs $= \left[\frac{1}{8} \times 8 + \frac{1}{2} \times 6\right] + \underbrace{\left[1 \times 4\right]}_{\text{Alternate TVs}} = 8$

The C-atom in TVs touches its four surrounding atoms (nearest neighbours), so the coordination number = 4.

The carbon atoms in an fcc lattice do not touch atoms at all. But C-atoms which are present in tetrahedral voids touch the surrounding four atoms. So, the centre-to-centre distance between two C-atoms is:

$$2r = \frac{\sqrt{3}}{4}a \implies r = \frac{\sqrt{3}}{8}a.$$

where a is the length of the unit cell and r is the radius of C-atom.

Packing efficiency (PE) of diamond cubic (dc)

$$PE = \frac{Z_{\text{eff}} \times \text{Volume of C-atom}}{a^3} \times 100$$

$$= \frac{8 \times \frac{4}{3} \pi r^3 \times 100}{a^3} \left(r = \frac{\sqrt{3}a}{8} \right)^3$$

$$= \frac{8 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{8} \right)^3 \cancel{a}^3 \times 100}{\cancel{a}^3}$$

$$= \frac{32}{3} \pi \left(\frac{\sqrt{3}}{4} \right)^3 \times 100 = 34\%$$

Germanium, silicon, and grey tin also crystallize in the same way as diamond does.

1.18 SPINEL STRUCTURES

Spinel structures are examples of an ionic crystal with more than two types of ions. Spinels are compounds with two different cations A²⁺ and B³⁺ and oxide (O²⁻) as the anion, with the general formula $A^{+2} B_2^{+3} O_4^{-2}$.

Note: Many substances of the type (A⁴⁺ B₂²⁺O₄²⁻) also have spinel-type structure.

1.18.1 NORMAL SPINEL STRUCTURES

In such structures, O²⁻ anions form the fcc packing and 1/8th of TVs are occupied by divalent metal ion A²⁺ and half of the octahedral voids are occupied by trivalent metal ions (B3+). the unit cell, we have

 $Z_{\rm eff}$ of ${
m O}^{2-}$ anion in fcc packing = 4/unit cell Number of TVs = 8/unit cell Number of $OV_S = 4/unit$ cell

Number of A^{2+} ions = $\frac{1}{9} \times TVs = \frac{1}{9} \times 8 = 1$ Number of B³⁺ ions = $\frac{1}{2} \times \text{OVs} = \frac{1}{2} \times 4 = 2$

General formula = $A_1^{2+} B_2^{3+} O_4^{2-} \equiv AB_2O_4$ Examples: $ZnAl_2O_4$, $MgAl_2O_4$, $ZnFe_2O_4$.

Alternatively

Let Z_{eff} of O^{2-} anion in fcc packing = 1/atomNumber of $TV_S = 2/atom$ Number of $OV_S = 1/atom$

Number of A²⁺ ions = $\frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 2 = \frac{1}{4}$ Number of B³⁺ ions = $\frac{1}{2} \times OVs = \frac{1}{2} \times 1 = \frac{1}{2}$

General formula:

$$A_{\frac{1}{4}}^{2+}B_{\frac{1}{2}}^{3+}O_{1}^{2-}$$

On simplifying, we get the formula AB2O4.

a. Ratio of TV/OV occupied in spinel structure Number of TV occupied = 1

Number of OVs occupied = 2

Ratio $\left(\frac{\text{TV}}{\text{OV}}\right)_{\text{accurated}} = \frac{1}{2} = 1:2$

b. Ratio of TV/OV unoccupied in spinel structure

Number of TVs unoccupied = 8 - 1 = 7Number of OVs unoccupied = 4 - 2 = 2

Ratio $\left(\frac{TV}{OV}\right)_{\text{unoccupied}} = \frac{7}{2} = 7:2$

1.18.2 INVERSE SPINEL STRUCTURES

In such structures, O² anions form the fcc packing and 1/8th of the tetrahedral voids are occupied by divalent metal ion A²⁺. Trivalen metal ions B³⁺ are present in $\left(\frac{1}{8} \text{th TV} + \frac{1}{4} \text{th OV}\right)$. Thus, in the unit cell, we have

 Z_{eff} of O^{2-} anion in fcc packing = 4/unit cell Number of TVs = 8/unit cell

Number of OVs = 4/unit cell

Therefore,
Number of A²⁺ ions =
$$\frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 8 = 1$$

Number of B³⁺ ions = $\frac{1}{8} \times \text{TVs} + \frac{1}{4} \times \text{OVs}$
= $\frac{1}{8} \times 8 + \frac{1}{4} \times 4$

$$= 1 + 1 = 2$$

General formula:

$$A_1^{2+}B_2^{3+}O_4^{2-} \equiv AB_2O_4$$

Alternatively

Let Z_{eff} of O^{2-} anion in fcc packing = 1/atom

Number of TVs =
$$2/atom$$

Number of
$$OVs = 1/atom$$

Therefore,

Number of A²⁺ ions =
$$\frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 2 = \frac{1}{4}$$

Number of B³⁺ ions =
$$\frac{1}{8} \times \text{TVs} + \frac{1}{4} \times \text{OVs}$$

= $\frac{1}{8} \times 2 + \frac{1}{4} \times 1$
= $\frac{1}{4} + \frac{1}{4}$
= $\frac{2}{4} = \frac{1}{2}$

So, general formula:

$$A_{\frac{1}{4}}^{2+} B_{\frac{1}{2}}^{3+} O_{1}^{2-}$$

Simplifying, formula = AB_2O_4 .

a. Ratio of TV/OV occupied in inverse spinel structure

Number of TV occupied = 1 + 1 = 2

Number of OV occupied = 1

So, ratio
$$\left(\frac{\text{TV}}{\text{OV}}\right)_{\text{occupied}} = \frac{2}{1} = 2:1$$

This ratio $\left(\frac{TV}{OV}\right)_{occupied}$ in inverse spinel structure is

reverse to that of the spinel structure. Hence, this is called inverse spinel structure.

b. Ratio of TV/OV unoccupied in inverse spinel structure

Number of TVs unoccupied = 8 - 2 = 6

Number of OVs unoccupied = 4 - 1 = 3

So, ratio
$$\left(\frac{\text{TV}}{\text{OV}}\right)_{\text{unoccupied}} = \frac{6}{3} = 2:1$$

1.19 CORUNDUM STRUCTURE

In this structure, O^{2-} anions form hcp and cations A^{3+} are present in two-thirds of the octahedral voids. The general formula of a compound is A_2O_3 . Examples are Fe_2O_3 , Al_2O_3 , Cr_2O_3 .

Calculation of general formula

First method:

 Z_{eff} of O^{2-} in hcp packing = 6/unit cell

Number of TVs = 12/unit cell

Number of $OV_S = 6/unit cell$

Therefore,

Number of
$$A^{3+} = \frac{2}{3} \times OVs = \frac{2}{3} \times 6 = 4$$

General formula:

$$A_4^{3+}O_6^{2-}$$

Simplifying, formula is A₂O₃.

Second method:

Let Z_{eff} of $O^{2-} = 1/\text{atom}$

Number of $TV_s = 2/atom$

Number of $OV_S = 1/atom$

Therefore,

Number of
$$A^{3+} = \frac{2}{3} \times OVs = \frac{2}{3} \times 1 = \frac{2}{3}$$

General formula:

$$A_{\frac{2}{3}}^{3+} O_1^{2-}$$

Simplifying, formula is A₂O₃.

Coordination number of corundum

From the formula, the ligancy of $(A^{3+}: O^{2-})$ in A_2O_3 is 6:4.

Note: Ligancy of A^{3+} = Number of O^{2-} ions Ligancy of O^{2-} = Number of A^{+3} ions

1.19.1 STRUCTURE OF THE OXIDES OF IRON

Iron forms three important oxides which are FeO, Fe₂O₃, and Fe₃O₄. These compounds have non-stoichiometric composition and are easily oxidized or reduced into each other. These aspects are explained on the basis of their crystal structure as follows:

a. Structure of FeO: If the oxides ions (O²⁻) form a cubic close packing with all the octahedral voids occupied by Fe²⁺ ions, we will get a perfect rock salt (NaCl) lattice. The formula of the oxide then would be FeO. However, actually the oxide is found to be non-stoichiometric with the composition Fe_{0.95}O (called wustite). This structure can be explained by assuming that a small number of Fe²⁺ ions in these octahedral voids are replaced by Fe³⁺ ions (of course every three Fe²⁺ ions would be replaced by two Fe³⁺ ions to maintain electrical neutrality). Consequently, we get Fe-deficient crystals.

Formula

Number of
$$O^{2-}$$
 in ccp = 4/unit cell
Number of Fe^{+2} = Number of OVs = 4/unit cell
Formula = $Fe_{A}^{2+}O_{A}^{2-}$ = 4FeO

b. Structure of red brown $\alpha\text{-Fe}_2O_3$

It is an hcp lattice of O^{2-} ions with Fe^{+3} ions in two-thirds of the octahedral voids.

Formula

Number of O^{2-} in hcp = 6/unit cell

Number of OVs = 6/unit cell

Number of Fe³⁺ ions =
$$\frac{2}{3} \times \text{OVs}$$

= $\frac{2}{3} \times 6 = 4/\text{unit cell}$

$$Formula = Fe_4^{3+}O_6^{2-}$$

Simplifying: Fe₂O₃.

Alternatively

If all Fe²⁺ ions in FeO is replaced by Fe³⁺ ions, then as every three Fe⁺² ions can be replaced by two Fe³⁺ ions to maintain electrical neutrality, the ratio between Fe^{3+} and O^{2-} will now be 2:3 and not 1:1, we get the oxide Fe_2O_3 .

- c. Structure of γ -Fe₂O₃: If α -Fe₂O₃ is oxidized, γ -Fe₂O₃ is formed which has a ccp lattice of O2- ions with Fe3+ ions randomly distributed in both octahedral and tetrahedral voids.
- d. Structure of Fe₃O₄: Fe₃O₄ (magnetite) is formed as a black solid by igniting Fe₂O₃ at 1400°C. Fe₃O₄ is a mixed oxide Fe^{II}O·Fe₂^{III}O₃ or Fe^{II} Fe₂^{III}O₄ which has an inverse spinel structure.

It is a ccp lattice of O^{2-} with larger Fe^{2+} in 1/8th of tetrahedral voids. Fe³⁺ ions are present in 1/4th of octahedral voids and 1/8th of tetrahedral voids.

Formula

Number of O^{2-} in ccp lattice = 4/unit cell

Number of TVs and OVs, respectively, are 8 and 4 per unit cell.

Number of Fe²⁺ ions =
$$\frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 8 = 1$$

Number of Fe³⁺ ions = $\frac{1}{8} \times \text{TVs} + \frac{1}{4} \text{ OVs}$
= $\frac{1}{8} \times 8 + \frac{1}{4} \times 4$
= $1 + 1 = 2$

= 1 + 1 = 2
∴ General formula =
$$Fe_1^{2+} Fe_2^{3+} O_4^{2-} \equiv Fe_3 O_4$$

All these compounds are called ferrites, but they are now represented as mixed oxides.

e. Another example of the iron oxide structure is MgFe₂O₄, where Mg²⁺ ions replace Fe²⁺ ions of Fe₃O₄. In the so-called normal spinel structure of compounds of the general formula AB_2O_4 (e.g., $MgAl_2O_4$ and ferrites such as $ZnFe_2O_4$), the divalent cations (Mg²⁺, Fe²⁺) are in tetrahedral voids and the trivalent B³⁺ ions (Fe³⁺, Al³⁺) are in octahedral voids Many of the ferrites which possess spinel-type structure ata important magnetic materials used in telephone or memory loops in computer. Fe₃O₄ (magnetic) is the load stone u_{8ed} by ancient travellers to find the direction.

ILLUSTRATION 1.25

In a compound, oxide ions are arranged in ccp. One-sixth of the tetrahedral voids are occupied by cations (A) and one-third of OVs are occupied by cations (B). (a) What is the formula of the compound? (b) What are the charges on A and B?

Sol. a. First method

Number of O^{2-} ions in ccp = 4

Number of TVs = 8

Number of $OV_S = 4$

Number of cations $A = \frac{1}{6} \times TVs$

 $=\frac{1}{6}\times 8=\frac{4}{3}$

Number of cations $B = \frac{1}{3} \times OVs$ $=\frac{1}{3}\times 4=\frac{4}{3}$

Formula $A_{\frac{4}{3}} B_{\frac{4}{3}} O_4^{2-} \equiv ABO_3$

Second method

Let the number of O^{2-} in ccp = 1/atom

Number of TVs = 2/atom.

Number of OVs = 1/atom.

Number of cations $A = \frac{1}{6} \times TV = \frac{1}{6} \times 2 = \frac{1}{3}$

Number of cations B = $\frac{1}{3} \times OV = \frac{1}{3} \times 1 = \frac{1}{3}$

Thus, formula is: $A_{1/3} B_{1/3} O_1^{2-} \Rightarrow ABO_3$

b. Various possibilities of charge on A and B since charge on oxide ion is -2.

$$ABO_{3} \Rightarrow A^{3+} B^{3+} O_{3}^{2-}$$

$$A^{2+} B^{4+} O_{3}^{2-}$$

$$A^{4+} B^{2+} O_{3}^{2-}$$

$$A^{5+} B^{1+} O_{3}^{2-}$$

$$A^{1+} B^{5+} O_{3}^{2-}$$

ILLUSTRATION 1.26

A compound is made of two elements P and Q. Atoms Q are in ccp arrangement while atoms P occupy all the tetrahedral voids. What is the formula of the compound?

Sol. First method

Number of Q atoms in ccp = 4/unit cell

Number of TVs = 8/unit cell

Number of OVs = 4/unit cell

Number of P atoms = Number of TVs = 8 Thus formula = $P_8Q_4 \Rightarrow P_2Q$.

Second method

Let number of Q atoms in ccp = 1/atom

Number of TVs = 2/atom

Number of OVs = 1/atom

Number of P atoms = Number of TVs = 2

Thus, formula = P_2Q

ILLUSTRATION 1.27

Two ions A^{\oplus} and B^{\odot} have radii 88 and 200 pm, respectively. In the close-packed crystal of compound AB, predict coordination number of A^{\oplus} .

Sol.
$$\frac{r_{\oplus}}{r_{\odot}} = \frac{r(A^{\oplus})}{r(B^{\odot})} = \frac{88}{200} = 0.44$$

It lies in the range 0.414 to 0.732.

Hence, the coordination number of $A^{\oplus} = 6$.

ILLUSTRATION 1.28

If the close-packed cations in an AB-type solid have a radius of 75 pm, what would be the maximum and minimum sizes of the anions filling the voids?

Sol. For close-packed AB-type solid,

$$\frac{r_{\oplus}}{r_{\odot}} = 0.414 - 0.732$$

∴ Minimum value of
$$r_{\odot} = \frac{r_{\oplus}}{0.732}$$
$$= \frac{75}{0.732} \text{ pm} = 102.5 \text{ pm}$$

Maximum value of
$$r_{\odot} = \frac{r_{\oplus}}{0.414} = \frac{75}{0.414} = 181.2 \text{ pm}$$

ILLUSTRATION 1.29

If the radii of Mg^{2+} , Cs^{\oplus} , O^{2-} , S^{2-} , and Cl^{\odot} ions are 0.65, 1.69, 1.40, 1.84, and 1.81 Å, respectively, calculate the coordination number of the cations in the crystals of MgS, MgO, and CsCl.

Sol. CN of MgS

a.
$$\frac{\text{Mg}^{2+}}{\text{S}^{2-}} = \frac{0.65}{1.84} = 0.35$$

(Range lies between 0.225 and 0414)

$$\therefore$$
 CN = 4

b. In MgO:
$$\frac{\text{Mg}^{2+}}{\text{O}^{2-}} = \frac{0.65}{1.40} = 0.48$$

(Range lies between 0.414 and 0.732)

$$\therefore$$
 CN = 6

c. In CsCl =
$$\frac{\text{Cs}^{\oplus}}{\text{Cl}^{\ominus}} - \frac{1.69}{1.81} = 0.93$$

(Range lies between 0.732 and 1)

$$\therefore$$
 CN = 8

1.20 PEROVSKITE STRUCTURE

The perovskite structure is a cubic lattice, with Ba²⁺ ions occupying the corners of the unit cell, O²⁻ ions occupying the face centres, and Ti⁴⁺ ions occupying the centres of the unit cell (Fig 1.60). Thus, the formula is:

Number of Ba²⁺ ions =
$$\frac{1}{8} \times 8$$
 corners = 1

Number of Ti^{4+} ions = 1 body centre atom.

Number of
$$O^{2-}$$
 ions = 6 faces $\times \frac{1}{2}$ face centre share = 3

Therefore, the formula is:
$$Ba^{2+}Ti^{4+}O_3^{2-} \equiv BaTiO_3$$

a. Ti⁴⁺ ions are present at the body centre of the unit cell, therefore they are present in octahedral voids.

Thus, OVs at the centres of the unit cell constitute onefourth of all the octahedral voids in an fcc lattice.

[Since total OV = 4(1 at body centre + 12/4 at edge centres)]

- **b.** Ti^{4+} ions at the centre of a unit cell has six nearest neighbour O^{2-} ions.
- c. The other octahedral voids located at the centres of the edges of unit cell have six nearest neighbours each as the case with any octahedral voids

But two out of the six neighbours are Ba^{2+} ions and four are O^{2-} ions.

d. The proximity of two cations, Ba²⁺ and Ti⁴⁺ would be electrostatically unfavourable.

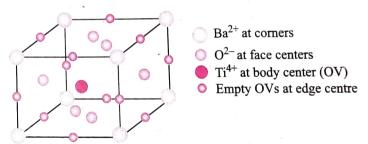


Fig. 1.60 Structure of perovskite

1.21 RUTILE STRUCTURE

TiO₂ exists in three forms called *anatase*, *brookite*, and *rutile*. The rutile structure is found in many crystals where the radius ratio is between 0.41 and 0.73.

It is not exactly a close-packed structure. Ti⁴⁺ ions in rutile are considered as forming a sufficiently distorted body centred cubic lattice (Fig. 1.61).

In rutile each Ti^{4+} ion is octahedrally surrounded by six O^{2-} ions whereas each O^{2-} is surrounded by only three Ti^{4+} ions arranged at the three corners of a plane triangle. The coordination numbers of Ti^{4+} and O^{2-} ions are 6 and 3, respectively.

:. Formula is:
$$Ti_3^{4+}O_6^{2-}$$
 or $2TiO_2$.

Note: CN of cation = Number of anions CN of anions = Number of cations

There are only a few cases where the radius ratio is below 0.41; examples are SiO_2 and BeF_2 . The coordination number of

 Si^{4+} and Be^{2+} is 4 and that of O^{2-} and F^{\odot} is 2. However, these are appreciably covalent.

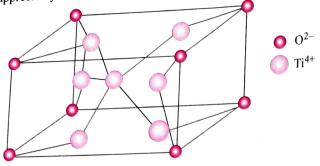
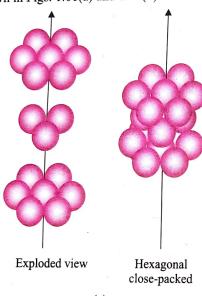


Fig. 1.61 Structure of rutile

1.22 CALCULATION OF EFFECTIVE ATOMS IN AN hcp UNIT CELL

The packing ABAB... is known as hcp packing. The unit cell of hep is shown in Figs. 1.61(a) and 1.61(b).



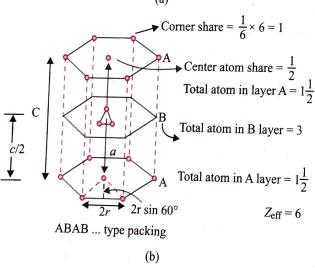


Fig. 1.62 ABAB... type packing

a. Number of effective atoms per unit cell

- Three atoms in B layer exclusively belong to this prism (i.e., in the body centre of hexagonal)
- ii. In layer A:
 - 1. One atom in the centre is shared by two prisms.
 - 2. There are 12 atoms in two A layers and each is shared

amongst six prisms of this type = $12 \times \frac{1}{6} = 2$ Z_{eff} in both A layers = 2 + 1 = 3.

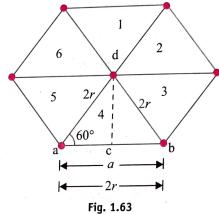
3. Z_{eff} in two A layers + Z_{eff} in B layer = 3 + 3 = 6 $\therefore Z_{\text{eff}} \text{ in hcp} = 6$

Alternatively

 $Z_{\text{eff}}/\text{unit cell} = 12 \times \frac{1}{6}$ (corner) (from both A l_{aye} + $2 \times \frac{1}{2}$ (in the centre of both A layers) + 3(in the body in layer B) \approx

b. Base area (A) of unit cell of hcp

It is equal to area of six equilateral triangles each with sid 2r and altitude (Fig. 1.63).



$$Sin 60^{\circ} = \frac{Perpendicular}{Hypotenuse} = \frac{cd}{ad}$$

$$\therefore P(\text{altitude}) = 2r \times \frac{\sqrt{3}}{2} = \sqrt{3}r$$

Base area,
$$A = 6 \times \frac{1}{2} (2r) \times \sqrt{3} r = 6\sqrt{3} r^2$$
(Learn it as a result

c. Calculation of height (c)

 $c = 2 \times \text{Distance}$ between close-packed layers

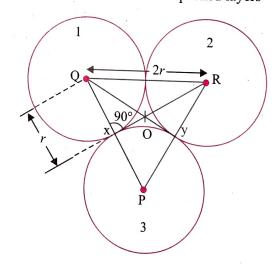


Fig. 1.64

i. Let us take three balls (1, 2, and 3) in the base layer A. Out of three medians in an equilateral ΔPQR , two medians Qy and Rx are shown in Fig. 1.64 intersecting at point O.

ii. In an equilateral Δ, medians are also perpendicular hisectors of sides, $\angle QxR = 90^{\circ}$ and Qx and Ry = r. In

$$(QR)^2 = (Qx)^2 + (xR)^2$$

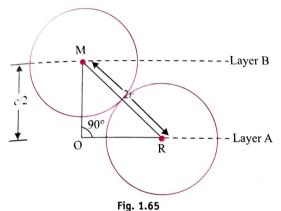
 $(2r)^2 = r^2 + (xR)^2 \Rightarrow xR = \sqrt{3}r$

 $(QR)^2 = (Qx)^2 + (xR)^2$ $(2r)^2 = r^2 + (xR)^2 \Rightarrow xR = \sqrt{3}r$ iii. Since medians intersect each other in the ratio of

$$RO = \frac{2}{3} xR \implies RO = \frac{2}{3} \sqrt{3} r = \frac{2r}{\sqrt{3}}$$

iv. Since distance between two layers A and B = c/2.

: In Fig. 1.65, point O is the intersection of medians.



In
$$\triangle$$
MOR,
 $(OM)^2 + (RO)^2 = (MR)^2$
 $\left(\frac{c}{2}\right)^2 + \left(\frac{2r}{\sqrt{2}}\right)^2 = (2r)^2$

$$\Rightarrow \left(\frac{c}{2}\right)^2 = \frac{8r^2}{3} \Rightarrow c = 4r\sqrt{\frac{2}{3}}$$
Hence, height $(c) = 4r \times \sqrt{\frac{2}{3}}$ or $2a \times \sqrt{\frac{2}{3}}$ $(\because a = 2r)$

(Learn it as a result.)

d. Volume of unit cell = Base area \times Height (c)

$$= 6\sqrt{3}r^2 \times 4r \times \sqrt{\frac{2}{3}} = 24\sqrt{2}r^3$$

(Learn it as a result.)

e. Packing fraction = $\frac{6 \times \text{Volume of atom}}{\text{Volume of unit cell}}$

$$= \frac{6 \times \frac{4}{3} \pi r^3}{24 \sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = \frac{3.143}{3 \times 1.414} = 0.74$$

: Packing efficiency = Packing fraction × 100 (or % of volume occupied) = $0.74 \times 100 = 74\%$ % of volume unoccupied (empty space) = 100 - 74= 26%

(Learn it as a result.)

Calculation of c/a ratio for ideally close-packed hcp crystal:

From the above in point c (iv), $c = 4r\sqrt{\frac{2}{3}}$ (: a = 2r)

$$\therefore \frac{c}{a} = \frac{4r}{2r} \sqrt{\frac{2}{3}} = 2 \times \sqrt{\frac{2}{3}} = 1.633$$
(Learn it as a result.)

Alternatively

The ABAB... type of stacking represents the hep structure joining the centres of three neighbouring atoms of the middle plane to the centres of the atoms of the top and bottom planes resulting in two tetrahedra with a common base (Fig. 1.66). The top and bottom atoms are centres at two lattice points, one above the other on the two hexagonal base planes of the unit cell. So, the distance between them is the unit distance along the c-axis. The distance between any two adjacent atoms of a plane is unit distance along the a-axis. Unit of c is equal to twice the normal from the apex of a tetrahedron to its base. The unit of a is equal to the side of the tetrahedron.

$$\frac{c}{a} = \frac{2PT}{RS}$$

$$RU = \sqrt{RS^2 - SU^2} = \sqrt{a^2 - (a^2/4)} = \sqrt{3}a/2$$

$$RT = \frac{2}{3}RU = \frac{a}{\sqrt{3}}$$

$$PT = \sqrt{PR^2 - RT^2} = \sqrt{a^2 - (a^2/3)} = a\sqrt{2}/\sqrt{3}$$

$$\frac{c}{a} = \frac{2\sqrt{2}}{\sqrt{3}} = 1.633$$

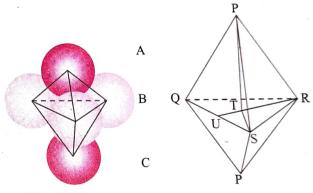


Fig. 1.66 In the ABAB... packing, which is hcp, the centres of three atoms Q, R, and S on plane B are joined to the centres of P atoms in plane A above and below

1.23 EFFECT OF TEMPERATURE AND PRESSURE ON A CRYSTAL **STRUCTURE**

A number of metals have more than one crystal form, iron, for example, is bcc at room temperature and changes over to the fcc form at 910°C. At 1410°C, iron again changes over to the bcc form. In general, at higher temperatures, bcc crystal structure is to be expected as it allows larger vibrational amplitudes for atoms, thereby increasing the entropy and lowering the free energy of the crystal. This is believed to be the reason for a number of alkali metals adopting the bcc form at room temperature.

At ordinary temperatures and pressures, chlorides, bromides, and iodides of lithium, sodium, and rubidium and some halides of silver possess the NaCl structure with 6: 6 coordination. On the application of high pressure, they transform to the CsCl structure with 8:8 coordination. On the other hand, CsCl on heating transforms to the NaCl structure with 6: 6 coordination.

Pressure CsCl-type structure NaCl-type structure = 760 K (8:8) coordination (6:6 coordination)

ILLUSTRATION 1.30

Whenever a two-dimensional square packing same layers are kept in the way so that the centres are aligned in all three dimensions, coordination number of each sphere is

c. 12

d. 10

Sol. a. The coordination number is 6. ("4 atoms" in the plane +1 atom above +1 atom below the particular atom).

ILLUSTRATION 1.31

In an fcc crystal, which of the following shaded planes contain the given (→) type of arrangement of atoms?





b.







Sol. a.

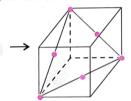


ILLUSTRATION 1.32

In hexagonal close packing of sphere in three dimensions.

- a. In one unit cell there are 12 octahedral voids and all are completely inside the unit cell.
- b. In one unit cell there are six octahedral voids and all are completely inside the unit cell.
- c. In one unit cell there are six octahedral voids and of which three are completely inside the unit cell and other three are from contributions of octahedral voids which are partially inside the unit cell.
- d. In one unit cell there are 12 tetrahedral voids, all are completely inside the unit cell.

Sol. b. hcp = AB AB AB... pattern repeat

For calculating voids between two layers A and B.

Total tetrahedral voids = 12 (represented by "o") out of which 8 are completely inside but rest are shared by other unit cells.

Total octahedral voids = 6 (represented by "•"). All a completely inside.

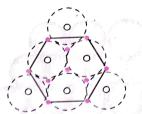
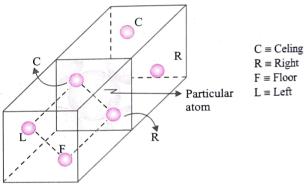


ILLUSTRATION 1.33

The coordination number of an fcc structure for a metal is 12

- a. Each atom touches four others in same layer, two in layer above and six in layer below.
- b. Each atom touches four others in same layer, four in laver above and four in layer below.
- c. Each atom touches six others in same layer, three in laver above and three in layer below.
- d. Each atom touches eight others in same layer, two in layer above and two in layer below.

Sol. a.



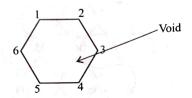
Each atom touches 4 atoms in the same layer, 4 in above layer and 4 in layer below.

ILLUSTRATION 1.34

Which of the following statements is correct for a twodimensional hexagonal close-packed layer?

- a. Each sphere is surrounded by six spheres
- b. Each sphere is surrounded by six voids
- c. Each sphere has three voids
- d. Each void is surrounded by three spheres

Sol. (a, b, d)



- a. Each sphere is surrounded by six spheres.
- b. Each sphere is surrounded by six voids.
- c. Effective number of atoms in a hexagonal unit cell

$$= \left(\frac{1}{3} \times 6\right) \times (1 \times 1) = 3$$

Effective number of voids in a hexagonal unit cell = 6 Hence, each sphere has two voids.

d. Each void is surrounded by three spheres.

ILLUSTRATION 1.35

A compound made of particles A, B, and C forms ccp lattice. Ions A are at lattice points, B occupy TVs and C occupy OVs. If all the ions along one of the edge axis are removed, then the formula of the compound is

d.
$$A_4B_{3.75}C_8$$

Sol. a. Since lattice is ccp,
$$Z_{\text{eff}} = 4$$
.

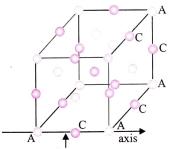
 \therefore Number of A ions = 4

$$(corner + face centre = 1 + 3 = 4)$$

Number of B ions = Number of TVs = 8

Number of C ions = Number of OVs = 4

- 2 TVs are formed at each body diagonal of cube.
- 4 TVs are formed on edge centres and body centre.



(Axis passing through one of the edges)

- A ions are at corner + face center
- C ions are at edge center and body center (where OVs are formed)
- 2 B ions (not shown in the figure) are at four-body diagonal

2 A ions (at corner) and one C ion (at edge centre are removed.

Number of A ions removed = $2 \times \frac{1}{8}$ (corner share) = $\frac{1}{4}$

Number of C ions removed = $1 \times \frac{1}{4}$ (edge centre share) = $\frac{1}{4}$

Number of A ions left = $4 - \frac{1}{4} = 3.75$

Number of B ions = 8

(Since no B ion has been removed)

Number of C ions left = $4 - \frac{1}{4} = 3.75$ Thus, formula is: $A_{3.75}B_8C_{3.75}$

ILLUSTRATION 1.36

A compound made of particles A, B, and C forms ccp lattice. In the lattice, ions A occupy the lattice points and ions B and C occupy the alternate TVs. If all the ions along one of the body diagonals are removed, then formula of the compound is

a.
$$A_{3.75}B_3C_3$$

b.
$$A_{3.75}B_3C_4$$

c.
$$A_3B_{3.75}C_3$$

d.
$$A_3B_3C_{3.75}$$

Sol. a. Since the lattice is $ccp (Z_{eff} = 4)$.

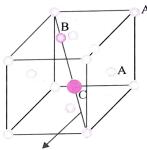
 \therefore Number of A ions = 4

$$(corner + face centre = 1 + 3 = 4)$$

Number of B ions = Number of alternate
$$TV = 4$$

Number of C ions = Number of alternate
$$TV = 4$$
.

Number of A ions removed =
$$2 \times \frac{1}{8}$$
 (corner share) = $\frac{1}{4}$



One of the body diagonals. Other diagonals are not shown in the figure

- A ions are at corner + face center
- B ions are at alternate TV at each of the 4 body diagonal
- C ions are also at alternate TVs at each of the four body diagonals

Number of B ions removed = 1

Number of C ions removed = 1

(Since body diagonal ions are inside the cube so they do not share with other ions).

Number of A ions left = $4 - \frac{1}{4} = 3.75$

Number of B ions left = 4 - 1 = 3

Number of C ions left = 4 - 1 = 3

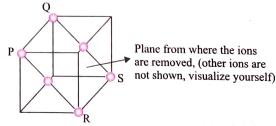
Thus, formula is: $A_{3.75}B_3C_3$

ILLUSTRATION 1.37

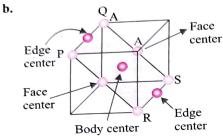
A compound is made of particles A and B. A forms fcc packing and B occupies all the OVs. If all the particles along the plane as shown in the figure below are removed, then the simplest formula of the compound is

$$\mathbf{a.} \, \mathbf{A_5} \, \mathbf{B_7}$$

$$\mathbf{b}$$
, \mathbf{A}_7 \mathbf{B}_5



Sol. c. Since the lattice is fcc ($Z_{eff} = 4$), therefore, number of A ions = 4 (1 corner + 3 face centre) Number of B ions = Number of $OV_S = 4$. (OVs are formed at body centre and edge centre). lons are removed from the plane (PQRS) as shown in the the figure. From the figure, it is clear, 4 corner ions and two edge centre ions on PQ and RS are also removed. Also two face centre ions lying on PR and QS along with one ion present in the body centre are removed as



shown in the figure below.

- 4 A ions from corner and 2 A ions from face center (PR and QS are removed)
- 2 B ions from edge center (PQ and RS) and one ion from body center are removed

.. Number of A ions removed

=
$$4 \times \frac{1}{8}$$
 (corner share) + $2 \times \frac{1}{2}$ (face centre share)

$$= \frac{1}{2} + 1 = 1\frac{1}{2}.$$

Number of B ions removed

=
$$2 \times \frac{1}{4}$$
 (edge centre share) + $\frac{1}{1}$ (body centre share)

$$= \frac{1}{2} + 1 = 1\frac{1}{2}$$

Number of A ions left = $4 - 1\frac{1}{2} = 2.5$

Number of B ions left = $4 - 1\frac{1}{2} = 2.5$

Thus, formula = $A_{2.5}B_{2.5} = 2.5AB$

Simplest formula = AB

ILLUSTRATION 1.38

In a solid having rock salt structure, if all the atoms touching one body diagonal plane are removed (except at body centre), then the formula of the left unit cell is

a.
$$A_{3.5}B_{2.5}$$

$$\mathbf{d.} \mathbf{A_3} \mathbf{B_5}$$

Sol. a. NaCl (rock salt)-type structure is fcc type.

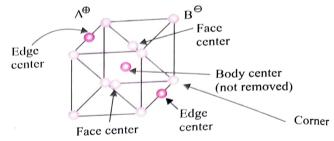
$$(:. Z_{\text{eff}} = 4)$$
 $[Z_{\text{eff}}(\text{Na}^{\oplus}) = 4, Z_{\text{eff}}(\text{Cl}^{\ominus}) = 4]$

In NaCl structure anion (Cl^{\odot}) (here B^{\odot}) are present at corners and face centre while cations (Na^{\Theta}) (here A^{\Theta}) are present in all OVs (present at body centre and edge centre).

.. Number of B[©] ions removed

=
$$4 \times \frac{1}{8}$$
 (corner share) + $2 \times \frac{1}{2}$ (face centre share)

$$= \frac{1}{2} + 1 = 3/2$$



4 B^Θ from corner and 2 B^Θ from face center are removed.

○ 2 A[⊕] from edge center are removed (body centered is)

Number of A^{\oplus} ions removed = $2 \times \frac{1}{4}$ (edge centre share) = $\frac{1}{4}$

Note: Body centre A[®] ion is not removed.

:. Number of B^{$$\odot$$} ions left = $4 - \frac{3}{2} = \frac{5}{2} = 2.5$

Number of A^{$$\oplus$$} ions left = $4 - \frac{1}{2} = \frac{7}{2} = 3.5$

Thus, formula is: A_{3.5}B_{2.5}.

ILLUSTRATION 1.39

Calculate the value of Avogadro's number from the following data

Density of NaCl = 2.165 g cm^{-3}

Distance between Na[⊕] and Cl[⊙] in NaCl = 281 pm

Sol. A unit cell of NaCl contains four NaCl units.

$$\therefore Z_{\text{eff}} = 4, Mw = 23 + 35.5 = 58.5,$$

$$\rho = 2.165 \text{ g cm}^{-3} \text{ (given)}$$

As distance between Na[⊕] and Cl[⊙] in NaCl = 281 pm

 \therefore Edge of the unit cell = $2 \times 281 = 562$ pm

Substituting these values in the expression

$$\rho = \frac{Z_{\text{eff}} \times Mw}{a^3 \times N_{\text{A}} \times 10^{-30}}$$

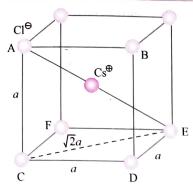
$$2.165 = \frac{4 \times 58.5}{(562)^3 \times N_A \times 10^{-30}}$$

$$N_{\Lambda} = 6.09 \times 10^{23}$$

ILLUSTRATION 1.40

CsCl has bee arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

Sol. The bcc arrangement of CsCl is shown in the figure below The aim is to find half of the body diagonal AE. If the edge of the unit cell is a, then



CE =
$$\sqrt{a^2 + a^2} = \sqrt{2}a$$

 \therefore AE = $\sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$
= $\sqrt{3} \times 400$
 \therefore Interionic distance = $\frac{1}{2}$ AE
= $\sqrt{3} \times 200 = 346.4$ pm

ILLUSTRATION 1.41

A solid AB has CsCl-type structure. The edge length of the unit cell is 404 pm. Calculate the distance of closest approach between A^{\oplus} and B^{\odot} ions.

Sol. The distance of closest approach is equal to the distance between the nearest neighbours (d). As CsCl has bcc lattice,

$$d = \frac{\sqrt{3}}{2} a = \frac{1.732}{2} \times 404 \text{ pm} = 349.9 \text{ pm}$$

ILLUSTRATION 1.42

CsCl has cubic structure. Its density is 3.99 g cm⁻³. What is the distance between Cs^{\oplus} and Cl^{\odot} ions? (Atomic mass of Cs = 133)

Sol. CsCl has bcc structure, so $Z_{\text{eff}} = 1$

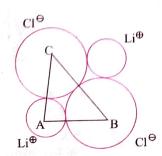
$$\rho = \frac{Z_{\text{eff}} \times Mw}{a^3 \times 10^{-30} \times N_{\text{A}}} \text{ or } a^3 = \frac{Z_{\text{eff}} \times Mw}{\rho^3 \times 10^{-30} \times N_{\text{A}}}$$
$$= \frac{1 \times (133 + 35.5)}{3.99 \times 10^{-30} \times 6.02 \times 10^{23}}$$
$$= 70.15 \times 10^6$$

$$a = (70.15)^{1/3} \times 10^{2}$$

$$= 4.12 \times 10^{2} \text{ pm} = 412 \text{ pm}$$
Interionic distance = $\frac{\sqrt{3}a}{2} = \frac{1.732}{2} \times 412 = 356.8 \text{ pm}$

ILLUSTRATION 1.43

The unit cube length for LiCl (NaCl structure) is 5.14 Å. Assuming anion—anion contact, calculate the ionic radius for chloride ion.



Sol. Interionic distance of LiCl

$$= \frac{5.14}{2} = 2.57 \text{ Å}$$

$$\therefore BC = \sqrt{AB^2 + AC^2} = \sqrt{(2.57)^2 + (2.57)^2} = 3.63$$
Radius of Cl[©] ion = $\frac{1}{2} \times 3.63 = 1.81 \text{ Å}$

ILLUSTRATION 1.44

Cesium may be considered to form interpenetrating simple primitive cubic crystal. The edge length of unit cell is 412 pm. Determine

- a. The density of CsCl.
- **b.** The ionic radius of Cs^{\oplus} if the ionic radius of Cl^{\ominus} is 181 pm. Given: Aw (Cs) = 133 g mol⁻¹.

Sol. The interpenetrating simple primitive cubic crystals mean the unit cell is body-centred where Cl^{\ominus} ions occupy corners and Cs^{\oplus} ions occupy body centre of the cube. There is one Cs^{\oplus} ion and one Cl^{\ominus} ion (or one molecule of CsCl) per unit cell.

From the expression,
$$\rho = \frac{Z_{\text{eff}} \times Aw}{a^3 \times N_A}$$

$$= \frac{1}{(412 \times 10^{-12} \text{ m})^3} \left(\frac{133.0 \text{ g mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} \right)$$

$$= 0.4 \times 10^7 \text{ g m}^{-3} \equiv 4.0 \text{ g cm}^{-3}$$

Now since Cs[⊕] ions touch the two chlorides along the cross diagonal of the cube, we will have

$$2r_{c} + 2r_{a} = \sqrt{3} a$$

or $r_{c} = \left(\frac{\sqrt{3}}{2}\right) a - r_{a} = \left(\frac{\sqrt{3}}{2}\right) (412 \text{ pm}) - (181 \text{ pm})$
= 175.8 pm

ILLUSTRATION 1.45

KCl crystallizes in the same type of lattice as does NaCl. Given that

$$\frac{r_{\text{Na}^{\oplus}}}{r_{\text{Cl}^{\odot}}} = 0.5 \text{ and } \frac{r_{\text{Na}^{\oplus}}}{r_{\text{K}^{\oplus}}} = 0.7$$

Calculate (a) the ratio of side of the unit cell for KCl to that for NaCl, and (b) the ratio of density of NaCl to that of KCl.

Sol. NaCl crystallizes in the face-centred cubic unit cell, such that

$$r_{\text{Na}} + r_{\text{Cl}} = a/2$$

where a is the edge length of unit cell. Now since $r_{\text{Na}\oplus}/r_{\text{Cl}}=0.5$ and $r_{\text{Na}\oplus}/r_{\text{K}\oplus}=0.7$, we will have

$$\frac{r_{\text{Na}^{\oplus}} + r_{\text{Cl}^{\odot}}}{r_{\text{Cl}^{\odot}}} = 1.5$$

$$\left[\frac{r_{\text{Na}^{\oplus}}}{r_{\text{Cl}^{\odot}}} + 1 = 0.5 + 1\right]$$

and
$$\frac{r_{K^{\oplus}}}{r_{Cl^{\ominus}}} = \frac{r_{K^{\oplus}}}{r_{Na^{\oplus}}/0.5} = \frac{0.5}{r_{Na^{\oplus}}/r_{K^{\oplus}}} = \frac{0.5}{0.7}$$

[Add 1 to both sides]

or
$$\frac{r_{\text{K}^{\oplus}} + r_{\text{Cl}^{\odot}}}{r_{\text{Na}^{\oplus}} + r_{\text{Cl}^{\odot}}} = \frac{1.2}{0.7} \times \frac{1}{1.5}$$

or
$$\frac{a_{\text{KCl}}/2}{a_{\text{NaCl}}/2} = \frac{1.2}{0.7 \times 1.5}$$

or
$$\frac{a_{\text{KCl}}}{a_{\text{NaCl}}} = \frac{1.2}{1.05} = 1.143$$

Now since
$$\rho = \frac{Z_{\text{eff}}}{a^3} \left(\frac{Mw}{N_A} \right)$$

We will have
$$\frac{\rho_{\text{NaCl}}}{\rho_{\text{KCl}}} = \left(\frac{a_{\text{KCl}}}{a_{\text{NaCl}}}\right)^3 \frac{Mw_{\text{(NaCl)}}}{Mw_{\text{(KCl)}}}$$
$$= (1.143)^3 \left(\frac{58.5}{74.5}\right) = 1.172$$

ILLUSTRATION 1.46

LiI occurs as cubical closed packing. If the edge length of unit cell is 624 pm, determine the ionic radii of Li^{\oplus} and I^{\odot} ions.

Sol. The cubical closed packing has a face-centred cubic unit cell. I^{\odot} ions occupy the corners and the face centres. These ions touch each other along the face diagonal of the cube. Hence

$$4r_{\rm I\odot}=\sqrt{2}\,a$$

$$r_{\text{I}\odot} = \frac{a}{2\sqrt{2}} = \frac{624 \text{ pm}}{2(1.414)} = 220.65 \text{ pm}$$

Now along the edge, we will have I^{\ominus} in Li^{\oplus} I^{\ominus} arrangement, where I^{\ominus} ions are at the corners and Li^{\oplus} ions at the centre of the edge (octahedral void). Since in closest packing, they touch each other, we will have

$$2r_{\mathrm{I}^{\ominus}}+2r_{\mathrm{Li}^{\oplus}}=a$$

or
$$r_{\text{Li}} = \frac{a}{2} - r_{\text{I}} = \frac{624 \text{ pm}}{2} - 220.65 \text{ pm} = 91.35 \text{ pm}$$

ILLUSTRATION 1.47

The composition of a sample of Wustite is Fe_{0.93}O_{1.00}. What percentage of the iron is present in the form of Fe (III)?

Sol. First method

Oxidation number (ON) of Fe in Fe_{0.93}O

$$= 0.93 \times X - 2 \times 1 = 0 \Rightarrow X = 2.15$$

Oxidation number (ON) of Fe is an intermediate value of Fe $^{2^+}$ and Fe $^{3^+}$

Let % of
$$Fe^{3+} = a$$

$$\frac{3 \times a + 2(100 - a)}{100} = 2.15 \Rightarrow a = 15.05\%$$

:. Percent of
$$Fe^{3+} = 15.05$$
 % of $Fe^{+2} = 84.95$

Second method

Let X atoms of Fe^{3+} ions are present in the compounds.

∴ Fe_{0.93} (Number of Fe³⁺ ions + Number of Fe²⁺ ions)
Number of Fe²⁺ ions = Total – Number of Fe³⁺
=
$$(0.93 - X)$$

Total positive charge (i.e., on $Fe^{2+} + Fe^{3+}$) = Total (negative charge on oxygen

$$2(0.93 - X) + 3X = 2 \Rightarrow X = 0.14$$

$$\therefore \text{ Percent of Fe}^{3+} = 0.14/0.93 \times 100 = 15.05$$

ILLUSTRATION 1.48

CsBr crystallizes in a body-centred cubic unit lattice with an edge length of 4.287 Å. Calculate the angles at which the second-order reflection maxima may be expected for (2, 0, 0), (1, 1, 0), and (1, 1, 1) planes when X-rays of $\lambda = 0.50$ Å are used.

Sol. For bcc lattice,
$$d_{200} = a/2$$

So, for second-order reflection,
$$2\lambda = 2 \times \frac{a}{2} \sin \theta_1$$

or $\sin \theta_1 = \frac{2\lambda}{a}$

i.e.,
$$\sin \theta_1 = \frac{2 \times 0.50}{4.287}$$
 and $\theta_1 = 13^{\circ}29'$

$$d_{110} = \frac{a}{\sqrt{2}}$$

So,
$$2\lambda = 2 \times \frac{a}{\sqrt{2}} \sin \theta_2 \Rightarrow \sin \theta_2 = \frac{\sqrt{2}\lambda}{a}$$
.

$$\sin \theta_2 = \frac{\sqrt{2} \times 0.50}{4.284} \Longrightarrow \theta_2 = 9^\circ 30'$$

$$d_{111} = \frac{a}{2\sqrt{3}}$$
, so $2\lambda = 2 \times \frac{a}{2\sqrt{3}} \sin \theta_3 \Rightarrow \sin \theta_3 = \frac{2\sqrt{3}\lambda}{a}$

i.e.,
$$\sin \theta_3 = \frac{2 \times \sqrt{3} \times 0.50}{4.287}$$
 and $\theta_3 = 23^{\circ}49'$

1.24 HAUY'S LAW OF RATIONAL INDICES

Hauy's law states that the intercepts of any face of a crystal along the crystallographic axes are either equal to the unit intercepts (a. b, c) or some simple whole number multiples of them, e.g., na, n'b, n''c, etc., where, n, n', n'', etc., are simple whole numbers Let OX, OY, and OZ represent the three crystallographic axes and let ABC be a unit plane.

The unit intercepts will then be a, b, and c (Fig. 1.67).

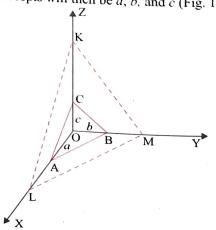


Fig. 1.67 Intercept of crystallographic plane

According to the above law, the intercept of any faces such as KLM, on the same three axes will be simple whole number multiples of a, b, and c, respectively. As can be seen from the figure, the simple multiples of this case are 2, 2, and 3.

1.24.1 WEISS INDICES

(9)

The coefficients a, b, c, i.e., l, m, n are known as weiss indices of a plane. For example, for a crystal plane which cut through the crystal axes at (2a, 3b, c), the weiss indices are 2, 3, 1.

1.24.2 MILLER INDICES

Miller indices are a set of integers (h, k, l) which are used to describe a given plane in a crystal. The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on various axes.

Reciprocal of the weiss coefficients and multiplying through by the smallest number will express all the reciprocals as integers.

The actual lattice in a crystal of a given kind consists of a repetition of a unit cell of that kind all over in three-dimensional space. As already mentioned, there can only be a maximum of 32 elements of symmetry (point groups). Combining these with 14 Bravais lattices there can be 230 different arrangements known as space groups.

ILLUSTRATION 1.49

Calculate the miller indices of crystal planes which cut through the crystal axes at

ii.
$$(a, b, c)$$

iv.
$$(2a, -3b, -3c)$$

Sol. Following the procedure given above, we prepare the tables as follows:

i.	a	b	c	ii.	a	1
		3	_		1	
	1/2	1/3	1		1	
		2			1	

Hence, the miller indices Hence, the miller indices are are (326). (111).

Hence, the miller indices Hence, the miller indices are are (122). $(3\overline{2}\overline{2})$.

1.24.3 d-SPACINGS

The distance between two parallel planes in a cubic crystal (d-spacing) is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is the length of the side of the cube and h, k, and l are miller indices of the parallel planes.

For the planes (100), (110), and (111) in a cubic unit cell,

a. sc [Fig. 1.68(a)]

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a$$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \sqrt{3}$$

$$d_{100} : d_{110} : d_{111} = 1 : 0.71 : 0.58$$

b. fcc [Fig 1.68(b)]

$$\begin{split} d_{200} : d_{220} : d_{111} &= \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}} \\ &= \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} \\ &= 1 : 0.707 : 1.154 \\ \frac{1}{d_{200}} : \frac{1}{d_{220}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \frac{\sqrt{3}}{2} \end{split}$$

c. bcc [Fig. 1.68(c)]

$$\begin{aligned} d_{200} : d_{110} : d_{222} &= \frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}} \\ &= \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} \end{aligned}$$

= 1 : 1.404 : 0.577 $\begin{array}{c} \bullet & a \\ \bullet$

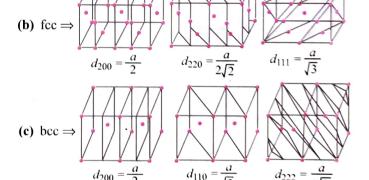


Fig. 1.68 Lattice plane separations for the cubic systems

1.24.4 INTERPLANAR DISTANCES FOR CUBIC SYSTEM

- **a.** (100) planes: Distance between these planes is equal to the length a of the side of cube, i.e., $d_{100} = a$.
- **b.** (200) planes: Distance between these planes is equal to the half length a/2 of the side of a cube, i.e., $d_{200} = a/2$.
- c. (110) planes: Spacing between these planes is one-half of the diagonal of the square base of the cube, i.e.,

$$d_{100} = (\sqrt{a^2 + a^2})/2 = a/\sqrt{2}.$$

d. (111) planes: The entire cross diagonal d of a cube spans three (111) planes. Thus, the distance between the two of each of these planes is d/3. Now,

$$d = \sqrt{a^2 + a^2 + a^2} = \sqrt{3} a$$

$$\therefore d_{111} = \frac{\sqrt{3} a}{3} = \frac{a}{\sqrt{3}}$$

e. (222) planes: These planes are in between (111) planes. Thus, the distance between any two such planes is

$$d_{222} = \frac{d_{111}}{2} = \frac{a}{2\sqrt{3}}$$

ILLUSTRATION 1.50

How do the spacings of the three planes 100, 110, and 111 of cubic lattice vary?

Sol. Applying the formula
$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}}$$

$$d_{100} = \frac{a}{\sqrt{(1^2 + 0^2 + 0^2)}} = a$$

$$d_{110} = \frac{a}{\sqrt{(1^2 + 1^2 + 0^2)}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{(1^2 + 1^2 + 1^2)}} = \frac{a}{\sqrt{3}}$$

Thus,
$$d_{100}: d_{110}: d_{111}:=1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}}=1:0.707:0.577$$

ILLUSTRATION 1.51

Potassium chloride crystallize with a body-centred cubic lattice. Calculate the distance between the 200, 110, and 222 planes. The length of the side of the unit cell is 5.34 Å.

Sol.
$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}}$$

For 200 plane
$$d_{200} = \frac{5.34}{\sqrt{(2^2 + 0^2 + 0^2)}} = \frac{5.34}{\sqrt{4}} = 2.67 \,\text{Å}$$

For 110 plane,
$$d_{110} = \frac{5.34}{\sqrt{(1^2 + 1^2 + 0^2)}} = \frac{5.34}{\sqrt{2}} = 3.77 \,\text{Å}$$

For 222 plane,
$$d_{222} = \frac{5.34}{\sqrt{(2^2 + 2^2 + 2^2)}} = \frac{5.34}{\sqrt{12}} = 1.54 \,\text{Å}$$

ILLUSTRATION 1.52

Diamond has face-centred cubic lattice. There are two atoms at (0, 0, 0) and $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ coordinates. The ratio of the carboncarbon bond distance to the edge of the unit cell is

a.
$$\sqrt{\frac{3}{16}}$$
 b. $\sqrt{\frac{1}{4}}$ **c.** $\frac{1}{4}$ **d.** $\frac{1}{\sqrt{2}}$

b.
$$\sqrt{\frac{1}{4}}$$

c.
$$\frac{1}{4}$$

d.
$$\frac{1}{\sqrt{2}}$$

Sol. a. Distance between (0, 0, 0) and $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right) = 2r$ $\Rightarrow 2r = \frac{\sqrt{3}a}{4}$ $\Rightarrow \frac{2r}{r} = \sqrt{\frac{3}{16}}$, where 2r = bond distance

ILLUSTRATION 1.53

Which of the following statements is(are) correct for the diamond

- a. Each atom has 4 nearest neighbours and 12 next nearest neighbours.
- b. It is relatively empty.
- c. The maximum proportion of the available volume which may be filled by hard spheres is only 0.34.
- d. The maximum proportion of the available volume which may be filled by hard spheres is only 0.46.

Sol. (a, b, c)

Atom (carbon) laying in the tetrahedral voids touches the surrounding 4 atoms at a distance of $\sqrt{3}a/4$, and the face centre atom has 12 next nearest neighbours at a distance of $a/\sqrt{2}$

For PF, refer section 1.17.

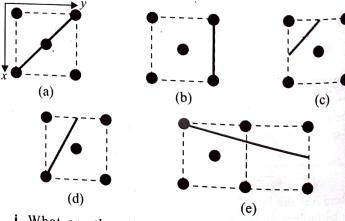
The packing fraction (PF) =
$$\frac{8 \times \frac{4}{3} \pi R^3}{a^3}$$

where
$$2R = \frac{\sqrt{3}a}{4} \Rightarrow \frac{R}{a} = \frac{\sqrt{3}}{8}$$

Hence, PF is:
$$\frac{32}{3} \pi \left(\frac{3\sqrt{3}}{8 \times 64} \right) = \frac{\sqrt{3}\pi}{16} \approx 0.34$$

ILLUSTRATION 1.54

Consider the two-dimensional "unit cell" shown in figure (a)-(e) below.



- i. What are the miller indices of the line shown in Fig. (a)?
 - a. 1, 1
- b. 1, 0
- c. 0, 1
- d. 2, 2

- ii. What are the miller indices of the line shown in Fig. (b)?
 - a. 1, 1
- b. 1, 0
- c. 0, 1
- d. 2, 2
- iii. What are the miller indices of the line shown in Fig. (c)?
 - a. 1, 1
- b. 1, 0
- c. 0, 1
- d. 2, 2
- iv. Which of the following sketches shows the 12 line in a two-dimensional unit cell?

 - a. Fig. a b. Fig. c
- c. Fig. d
- d. Fig. e
- v. Which of the following sketches shows the $(2, \overline{1})$ line in a two-dimensional unit cell?
 - a. All figures b. Fig. d
- c. Fig e
- d. None
- Sol. i. a. The miller indices are a set of integers hkl that are used to describe a given plane in a crystal. For this two-dimensional plane, only hk will be used. The procedure for determining the Miller indices for a plane is:
 - Prepare a table with the unit cell axes at the top of columns.
 - (II) Enter in each column the intercept (expressed as a multiple of a, b or c) of the plane with that axis.
 - (III) Invert all numbers
 - (IV) Clear fractions to obtain h, k, and l.

Table for Fig. (a)

a	b	
1	1	Intercepts
1	1	Reciprocals
1	1	Clear fraction

- : Miller indices as 1, 1.
- ii. c. Table for Fig. (b)

a	b			
œ	1	Intercepts		
0	1	Reciprocals		
0	1	Clear fractions		

- :. Miller indices as 0, 1.
- iii. d. Table for Fig. (c)

a	b	
1/2	1/2	Intercepts
2	2	Reciprocals
2	2	Clear fractions

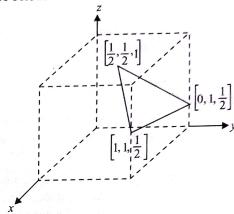
- : Miller indices as 2, 2.
- iv. c. The miller indices represent the number of equal segments into which each respective axis has been divided by the plane. For the 12th, line, the a-axis has been intersected at unity and the b-axis has been intersected into two equal segments. The line from

$$x = \frac{a}{l}$$
 to $y = \frac{b}{2}$, shown in Fig. (d), is the 12th line.

v. c. The bar over 1 in the set of indices represents -1. The $\overline{2}$ line divides the a axis into two equal segments and intersects the b axis at -b. The line from x = a/2 to y = -b/1 is shown in Fig. (e).

ILLUSTRATION 1.55

The coordinates of three corners of an octahedral face on a cubi unit cell are $\left(\frac{1}{2}, \frac{1}{2}, 1\right)$, $\left(0, 1, \frac{1}{2}\right)$ and $\left(1, 1, \frac{1}{2}\right)$ as shown in the figure below.



The miller indices of this plane is

- a. 0, 1, 1 b. 1, 0, 1
- c. 0, 0, 1
- d. 1, 1, 1
- Sol. a. The plane is shown in the figure above. The intercepts with the axes are ∞ , 2b, and 2c.

Table for the figure shown above:

a	b	c	
∞	2	2	Intercepts
0	1/2	1/2	Reciprocals
0	1	1	Clear fractions

:. Miller indices are 0, 1, 1.

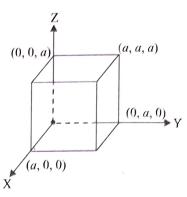
CONCEPT APPLICATION EXERCISE 1.1

- 1. A compound formed by elements X and Y crystallizes in the cubic structure when Y atoms are at the corners of the cube and X atoms are at the alternate faces. What is the formula of the compound?
- 2. Calculate the number of atoms in a cubic-based unit cell having one atom on each corner and two atoms one each diagonal.
- 3. A compound made up of elements A and B crystallizes in the cubic structures. Atoms A are present on the corners as well as face centres whereas atoms B are present on the edge centres as well as body centre. What is the formula of the compound? Draw the structure of its unit cell.
- 4. In an fcc arrangement of A and B atoms whose A atoms are at the corners of the unit cell and B atoms are at the face centres, one of the A atom is missing from one corner in each unit cell. What is the simplest formula of the compound?

- 5. A solid AB has NaCl structure. If the radius of the cation A is 100 pm, what is the radius of anion B?
- 6. In a crystalline solid, anions B are arranged in cubic close packing, cations A are equally distributed between octahedral and tetrahedral voids, what is the formula of the solid?
- 7. In sapphire, oxide ions are arranged in hexagonal close packing and aluminium ions occupy two-thirds of the octahedral voids. What is the formula of sapphire?
- 8. The density of NH₄Cl is 1.534 g cm⁻³. It crystallizes in the CsCl lattice.
 - (a) Calculate the length of the edge of NH₄Cl unit cell.
 - (b) Calculate the shortest distance between a NH_4^{\oplus} ion and a Cl^{Θ} ion.
 - (c) Calculate the radius of NH₄ ion if the radius of the Cl^{Θ} ion is 181 pm.
- 9. A solid A[⊕]B[⊙] has NaCl-type close-packed structure. If the radius of the cation is 90 pm, calculate the probable range of the radius of the anion.
- 10. A solid $A^{\oplus}B^{\ominus}$ has NaCl-type close-packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation? Can a cation C[®] having radius of 180 pm be slipped into the tetrahedral site of the crystal $A^{\oplus}B^{\odot}$? Give reason for your answer.
- 11. In a close-packed structure of oxides, one-eighth of the tetrahedral holes is occupied by bivalent cations (A) and half of the octahedral holes are occupied by trivalent cations (B), calculate the molecular formula of the oxide.
- 12. (a)MgO has the structure of NaCl and TlCl has the structure of CsCl. What are the coordination numbers of the ions in MgO and TlCl?
 - (b) If the closed-packed cations in an XY-type solid have a radius of 73.2 pm, what would be the maximum and minimum sizes of the anions filling voids?
 - (c) Fe₂O₃ (haematite) forms ccp arrangement of O²⁻ ions with Fe³⁺ ions occupying initerstitial positions. Predict whether Fe³⁺ ions are in the OV or TV. Given $r_{\text{Fe}^{3+}} = 0.7 \text{ Å and } r_{\text{O}^{2-}} = 1.4 \text{ Å}.$
 - (d) A solid XY has CsCl-type structure. The edge length of the unit cell is 400 pm. Calculate the distance of closest approach between X^{\oplus} and Y^{\ominus} ions.
- 13. Cadmium oxide crystallizes in NaCl type of crystal lattice. The compound is however usually non-stoichiometric with approximate formula CdO_{0.95.} The defect arises as some cationic positions are occupied by neutral Cd atoms instead of Cd2+ ions and equivalent numbers of anionic sites are vacant (Aw of Cd = $112.41 \text{ g mol}^{-1}$).
 - a. What percentage of anionic sites is vacant?
 - b. What is the density of non-stoichiometric solid (a = 470 pm)?
 - c. If the edge length of the unit cell is 470 pm, what would be the density of the perfect solid?

14. Assume an fcc unit cell cube (edge length a) with one of its corners at the origin of cartesian coordinates.

Find:



- a. The coordinates of TVs nearest and farthest to the origin.
- **b.** The distance between two successive TV_s
- The coordinates of OVs nearest and farthest to the origin
- d. The distance between two successive OVs.

1. XY **2.**
$$Z_{\text{eff}} = 9$$
 3. AB **4.** A_7B_{24} **5.** 241 pm **6.** A_2B **7.** AI_2O_3 **8. (a)** 387 pm **(b)** 335.1 pm **(c)** 154.1 pm

6.
$$A_2B$$
 7. Al_2O_3

12. (a) i.
$$CN \text{ of } Mg^{2+} = 6$$
 ii. $CN \text{ of } Tl^{\oplus} = 8$

$$CN = C^{2-}$$

$$CN \text{ of } O^{2-} = 6$$
 $CN \text{ of } Cl^{\Theta} = 8$

(b) 100 pm (min), 176.81 pm (max) **(c)** OVs **(d)** 346.4 pm

13. (a) 5% (b) 8.21 g cm^{-3} (c) 8.26 g cm^{-3}

14. (a) TV nearest =
$$\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$$
 (b) TV farthest = $\left(\frac{39}{4}, \frac{39}{4}, \frac{39}{4}\right)$

(c) OV nearest =
$$\left(0, \frac{a}{2}, 0\right); \left(\frac{a}{2}, 0, 0\right); \left(0, 0, \frac{a}{2}\right)$$

(d) OV farthest =
$$\left(\frac{a}{2}, a, a\right)$$
; $\left(a, \frac{a}{2}, a\right)$; $\left(a, a, \frac{a}{2}\right)$

1.25 POLYMORPHISM AND **ALLOTROPY**

Many solids exist only in one single crystalline form. However, many solids occur in more than one modification. For example, sodium chloride crystallizes as cubes. It can also be made to crystallize as octahedra. This occurrence of different crystal forms of the same substance is called polymorphism. Sodium chloride crystallizes as octahedra from an aqueous solution containing 15% urea. Interconversions of polymorphs take place at a given temperature. This is the transition temperature at the specified pressure at which the transition is studied. Some transitions are reversible, some are not.

Zinc blende (ZnS) $\xrightarrow{1024^{\circ}\text{C}}$ Wurtzite (ZnS)

Quartz (SiO₂)
$$\xrightarrow{870^{\circ}\text{C}}$$
 Tridymite (SiO₂) \rightleftharpoons

Cristobalite (SiO₂)

Polymorphism occurring in elements is commonly termed as allotropy. Three types of allotropy are distinguished depending on the method of transition from one to another: enantiotropy, monotropy, and dynamic allotropy.

If one modification is interconvertible to another at a fixed temperature (transition temperature) under a specified pressure, then this type of allotropy is termed as *enantiotropy*. The system rhombic and monoclinic sulphur exemplify this case. At 96.6°C, rhombic sulphur is converted to monoclinic and vice versa. Above 96.6°C, monoclinic sulphur is stable and below 96.6°C rhombic sulphur is stable.

Monotropic systems are systems where one modification is unstable at all temperatures and is converted to the stable form. Ozone–oxygen, red phosphorus–yellow phosphorus are such cases.

In dynamic allotropy, both forms exist side by side in equilibrium at all temperatures. A typical example of this case is λ - and μ -sulphur. The proportion of the two forms at equilibrium depends on temperature.

1.25.1 ISOMORPHISM AND ISOPOLYMORPHISM

Many pairs of compounds of similar composition are found to crystallize in the same form. Some common examples are:

- KH2PO4·H2O and KH2AsO4·H2O
- K₂SO₄ and K₂SeO₄
- \bullet CuSO₄·5H₂O and CuSeO₄·5H₂O
- • K_2SO_4 . $Al_2(SO_4)_3$ ·24 H_2O and K_2SO_4 · $Cr_2(SO_4)_3$ ·24 H_2O

The word "isomorphous" is applied to these substances. This may be stated as an equal number of atoms combined in the same way produce the same crystalline form. The crystalline form is independent of the chemical nature of the combined atoms.

Isomorphism can be detected by the following criteria:

- a. Similarity of crystalline form
- b. Formation of mixed crystals
- c. Formation of overgrowth

In case of polymorphic substances, if each of the two different forms of a polymorphic substance is isomorphous with a form of another polymorphic substance, then the phenomenon is termed as *isopolymorphism*.

Law of isomorphism

An isomorphic substance forms crystals which have the same shape and can grow in the saturated solution of each other. According to Mitscherlich, isomorphous substances have similar chemical constitution, i.e., they have the same number of atoms similarly arranged. Their formulae are, therefore, similar, for example, $\rm K_2SO_4$ and $\rm K_2CrO_4$ are isomorphous and so are $\rm ZnSO_4 \cdot 7H_2O$ and $\rm MgSO_4 \cdot 7H_2O$.

MnSO₄ shows three types of hydrated salts.

	Salt	Temp. of crystallization	Crystalline form
a.	MnSO ₄ ·7H ₂ O	Below 273 K	Rhombic like vitriol
	MnSO ₄ ·5H ₂ O		Asymmetric and isomorphous with CuSO ₄ ·5H ₂ O
c.	MnSO ₄ ·4H ₂ O	Above 298 K	Monosymmetric prism

ILLUSTRATION 1.56

Which of the following compounds are not isomorphous?

- a. Copper sulphate and zinc sulphate
- b. Zinc sulphate and manganeous sulphate
- c. Calcium carbonate and ferrous sulphate
- d. Zinc sulphate and ferrous sulphate

Sol.

- a. CuSO₄·5H₂O and ZnSO₄·7H₂O are not ismorphous. Different moles of H₂O.
- **b.** ZnSO₄·7H₂O and MnSO₄·7H₂O are isomorphous, with 7H₂O in both compounds.
- c. CaCO₃ and FeSO₄·7H₂O are not isomorphous, since the moles of H₂O are not same.
- **d.** $ZnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$ are isomorphous with same number of moles of H_2O .

ILLUSTRATION 1.57

Potassium selenate is isomorphous with potassium sulphate and contains 50.0% of Se. The atomic weight of Se is

Sol.

a. K_2SO_4 and potassium selenate are isomorphous. So the formula is K_2SeO_4 .

$$Mw \text{ of } K_2 \text{SeO}_4 = (39 \times 2 + x + 64)$$

= $(142 + x)g$

$$\therefore$$
 (142 + x) of $K_2 SeO_4 \Rightarrow x g$ of Se

100 g of
$$K_2 SeO_4 = \frac{x}{(142 + x)} \times 100$$

$$\therefore \frac{x \times 100}{(142 + x)} = 50$$

ILLUSTRATION 1.58

The Ew of an element is 13. It forms an acidic oxide which with KOH forms a salt isomorphous with K_2SO_4 . The Aw of element is

Sol. d. MSO_4 and K_2SO_4 are isomorphous. Thus, valency of S and M should be same = 6.

$$\therefore Aw = Ew \times \text{Valency}$$
$$= 13 \times 6 = 78.$$

1.26 IMPERFECTIONS IN SOLIDS

According to the Nernst law (third law of thermodynamics), true crystals possess perfect order of arrangement of atoms only at 0 K. But some deviation from complete order takes place with the increase in temperature. The presence of impurities also adds to imperfections in solids. These imperfections modify and impart new properties to the crystal.

Any departure from perfectly ordered arrangement of atoms/ions in a crystal is called imperfection or crystal defect.

There are three types of imperfections:

- a. Electronic imperfections
- b. Atomic or point defects
- c. Line defects or dislocations

1.26.1 ELECTRONIC IMPERFECTIONS

Electrons in ionic (e.g., NaCl) or covalent (e.g., Si) crystals occupy the lowest energy level at 0 K (absolute zero). Above 0 K, in pure Si or Ge, electrons are released from the covalent bonds. It leads to the presence of free electrons and electron-deficient bonds called holes, which are responsible for intrinsic conduction. These free electrons and holes in crystals are responsible for electronic imperfections.

Note:

- a. The following new terms will be used in this section:
 - i. Intrinsic conduction: Conduction which is caused in a crystal due to heating, leading to the formation of free electrons and holes, e.g., crystals of Si or Ge.
 - Hole: An electron-deficient bond formed by the release of an electron.
 - iii. n: Concentration of electrons (e)
 - iv. p: Concentration of holes (h).
- b. Atoms in a solid vibrate like a simple harmonic oscillator. They have different modes of vibration. When transition takes place from a higher vibrational state to a lower vibrational state, a quantum of thermal energy is emitted. This quantum number of thermal energy is called phonon in analogy to photon for light energy. Absorption of phonons by a crystal can produce atomic displacement leading to imperfection.

1.26.2 ATOMIC OR POINT DEFECTS

Crystalline solids have short-range as well as long-range order in the arrangement of their constituent particles, yet crystals are not perfect. A solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallization process occurs at fast or moderate rate. Single crystals are formed when the process of crystallization occurs at extremely slow rate. Even these crystals are not free of defects. The defects are basically irregularities in the arrangement of constituent particles. One such defect is point defect. Point defects are irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. Point defects are classified into three types: (a) stoichiometric defects, (b) non-stoichiometric defects, and (c) impurity defects.

Stoichiometric Defects

The point defects which do not disturb the stoichiometry of the solid are also called *intrinsic* or *thermodynamic defects*. Shown by non-ionic compounds, stoichiometric defects are of two types: vacancy defects and interstitial defects.

Vacancy defect

When some of the lattice sites are vacant, the crystal is said to have vacancy defect (Fig. 1.69). This results in a decrease in the

density of the substance. This defect can also develop $\widehat{w_{heh}}_{a}$ substance is heated.

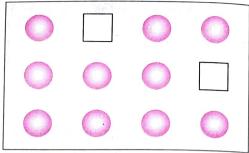


Fig. 1.69 Vacancy defects

Interstitial defect

When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect (Fig. 1.70). This defect increases the density of the substance. An important factor in determining the formation of interstitial defect is the size of the atom (or ion) because they are accommodated into the void.

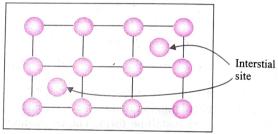


Fig. 1.70 Interstitial defects

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show defects such as Frenkel and Schottky defects.

Schottky defect

In ionic crystals of the type A^{\oplus} B^{\ominus} , equal number of anions and cations are missing from the lattice sites so that electrical neutrality is maintained. This type of defect is called Schottky defect (Fig. 1.71).

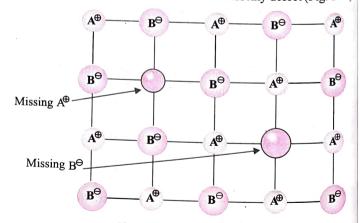


Fig. 1.71 Schottky defects

This type of defect is shown by highly ionic compounds which have high coordination number and cations and anions of similar sizes. For example, KCl, NaCl, AgBr, KBr, and CsCl.

Effects of Schottky defect

a. As the number of ions decreases and volume remains same, so the density decreases.

b. Crystals with Schottky defect conduct electricity to a small extent. This is because if an ion moves from its lattice site to occupy a "hole," it creates a new "hole." In this way, a hole moves across the crystal which as a result moves the charge in the opposite direction.

c. Due to the presence of holes, the stability (or lattice energy) of the crystal decreases.

Frenkel defect

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If an ion is missing from its lattice site (causing a vacancy or a hole there) and occupies an interstitial site so that the electrical neutrality as well as stoichiometry of the compound are maintained, this type of defect is called Frenkel defect (Fig. 1.72). Since the size of cations is generally smaller, it is more likely that cations occupy interstitial sites.

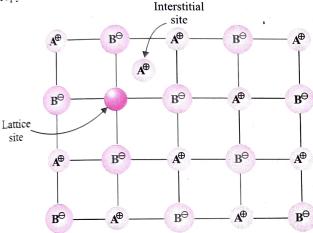


Fig. 1.72 Frenkel defect

Effects of Frenkel defect

i. This type of defect is present in those compounds which have low coordination number.

ii. Large difference in size of anion and cation, e.g., AgCl, AgBr, AgI, and ZnS.

iii. Solids with this defect conduct electricity to a small extent.

iv. The dielectric constant of the crystal increases.

v. The density of the solid is unchanged.

vi. Due to the presence of holes, the stability of the crystal decreases.

Note:

a. The above two defects are intrinsic defects, or thermodynamic defects. The number of defects increases with the increase in temperature, so are called thermodynamic defects. They are also called intrinsic defects because deviation from regular arrangement of atoms or ions occurs within the crystal and no external substance is added.

b. AgBr is a compound in which both Schottky and Frenkel defects are found because AgBr is highly ionic but there is a great difference in the size of Ag[⊕] and Br[⊙].

Calculation of number of Schottky/Frenkel defects

a. The number (n) of Schottky defects present in an ionic crystal containing N ions at temperature T is given by: $n = Ne^{-E/2KT,}$

where E is the energy required to create these n Schottky defects and K is the Boltzmann constant = R/N_A = 1.38 × 10²³ J K⁻¹

b. The number (n) of Frenkel defects in an ionic crystal containing N ions and N_i is the number of interstitial sites at a temperature T is given by:

$$n = (N/N_i)^{\frac{1}{2}} e^{-E/2KT}$$

(where E is the energy required to create n Frenkel defects. Knowing the value of E, the fraction n/N can be calculated, e.g., for NaCl at 1000 K, the energies of formation of these defects (i.e., Schottky and Frenkel, respectively) are 2 eV and 3 eV, respectively (1 eV = 1.602×10^{-19} J). AgBr has both Schottky and Frenkel defects. Both defects increase exponentially with increase in temperature.

In NaCl, there are 10²² ions and 10⁶ Schottky pairs/cm³ at room temperature, i.e., there is one Schottky pair defect per 10^{16} ions.

c. The fraction of the surface of a crystal vacancies is given

$$\frac{n}{N} = e^{-E/RT}$$

Table 1.13 Difference between Schottky and Frenkel defects

Schottky defect			Frenkel defect		
1.	It is due to equal number of cations and anions missing from the lattice sites.	1.	It is due to the missing of ions (usually cations) from the lattice sites and these occupy the interstitial sites.		
2.	This results in the decrease in the density of crystal.	2.	It has no effect on the density of crystal.		
3.	This type of defect is found in highly ionic compounds with high coordination number and having cations and anions of similar sizes, e.g., NaCl, CsCl, etc.	3.	This type of defect is found in crystal where the difference in the size of cations and anions is very large, e.g., AgCl, AgBr ZnS, etc.		

Non-Stoichiometric Defects

If an imperfection causes the ratio of cations and anions to become different from that indicated by the ideal chemical formula, the defect is called non-stoichiometric. Non-stoichiometric defects occurs as follows:

a. Metal excess defects

b. Metal deficiency defects

Metal excess defects

Metal excess defect may occur in either of the following two ways:

a. By anion vacancies or F-centre

A negative ion may be missing from its lattice site, leaving a hole, which is occupied by an electron thereby maintaining an electrical balance. The trapped electrons are called F-centres (from the German word Farbenzenter for colour centres) because they are responsible for imparting colour to the crystal Fig. 1.73. This defect is similar to Schottky defect and is found in crystals having Schottky defects.

Example: NaCl when heated in Na vapour atmosphere, the excess Na atom deposit on the surface. Now Cl[©] diffuse to the surface where they combine with Na atoms which lose the electrons. The electrons diffuse into the vacant sites created. The electrons absorb some energy from the visible light and re-emit the complimentary yellow colour to NaCl crystal. Excess of Li in LiCl gives a pink colour. Excess of K in KCl make it violet.

Fig. 1.73 An F-centre in a crystal

b. By the presence of extra cations in interstitial sites

Extra cations occupying interstitial sites with electrons present in another interstitial site to maintain electrical neutrality causes metal excess defects (Fig. 1.74). This defect is similar to Frenkel defect and is formed in crystals having Frenkel defects.

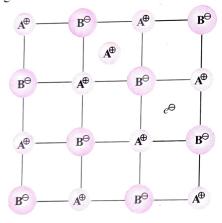


Fig. 1.74 Metal excess defect caused by extra cation in interstitial position

Example: If ZnO is heated, it loses oxygen and turns yellow. $ZnO \Longrightarrow Zn^{2+} + \frac{1}{2}O_2 + 2e^{-\frac{1}{2}}$

Now there is excess of Zn²⁺ in the crystal and its formula becomes $Zn_{(1+x)}O$.

The excess Zn²⁺ ions thus formed get trapped into the vacant interstitial sites while electrons are entrapped in the neighbouring interstitial sites these entrapped electrons increase the electrical conductivity of ZnO and turn yellow. On cooling, they again turn into white due to the reverse reaction as shown above.

Note: Crystals with either type of metal excess defect act as semiconductors.

Metal deficiency defects

This defect occurs when metals show variable valency. It occol due to the missing of a cation from its lattice site and presence, a cation with higher charge (e.g., ± 2 instead of ± 1) in the $\underset{adja_{Q_0}}{\text{adja}_{Q_0}}$ site (Fig. 1.75).

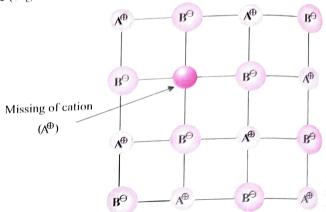


Fig. 1.75 Metal deficiency defect due to the missing of a cation of lowe valency and presence of a cation of higher valency

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metaas compared to the stoichiometric proportion. For example, Fel is found with a composition of Fe_{0.95}O. It ranges from Fe_{0.95}O. to Fe_{0.96}O. In the crystals of FeO, some Fe²⁺ cations are missing and the loss of positive charge is made up with the presence the required number of Fe³⁺ ions.

Example: Transition elements, FeO, FeS, and NiO.

Impurity Defects

These defects arise when foreign atoms are present at the lattice sites (in place of host atoms) or at the vacant interstitial sites. The formation of former depends upon the electronic structure of the impurity while that of the latter on the size of the impurity.

Introducing impurity defect in covalent solids

Group 13 elements such as Ga and Al and Group 15 elements such as P and As can enter the crystal structure of Group 14 element Ge or Si substitutionally.

Group 15 elements have one excess valence electrons compared to Group 14 elements (Si or Ge). Therefore, after forming four covalent bonds, one electron remains in excess which gives rise to electrical conduction.

Group 13 elements have one valence electron less compared Group 14 elements leading to electron-deficient bond or a hole Such holes can move across the crystal giving rise to electric conductivity.

Group-14 elements doped with Group 15 elements are called n-type semiconductors, where the symbol n indicating negative charge which flows in them. Group 14 elements doped wil group 13 elements are called p-type semiconductors, the symbol p indicating positive hole movement.

Introducing impurity defect in ionic solids

In case of ionic solids, the impurities are introduced by adding impurity of ions. If the impurity ions are in a different oxidation state from that of the host ions, vacancies are created (Fig. 1.76

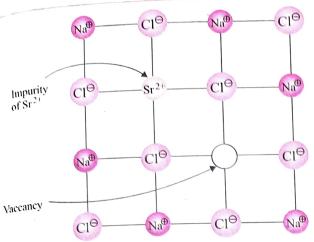


Fig. 1.76 Impurity defect

Example: If molten NaCl, containing a little of SrCl, as impurity, is allowed to cool, in the crystals of NaCl formed, at some lattice sites Na[®] ions are substituted by Sr²⁺ ions. For every Sr²⁺, thus introduced, two Na[®] ions are removed to maintain electrical neutrality, one of these lattice sites is occupied by Sr²⁺ ion and the other remains vacant. These vacancies result in the higher electrical conductivity of the solid.

1.26.3 LINE DEFECTS OR DISLOCATIONS

In addition to the point defects, many solids especially metals possess line defects or also called dislocations. The two important types of linear defects are edge dislocation and screw dislocation. Both result from the improper orientation of planes with respect to one another in the crystal.

An edge dislocation [Fig. 1.77(a)] is named so because due to his defect this edge of an atomic plane terminates within the crystal instead of passing all the way through.

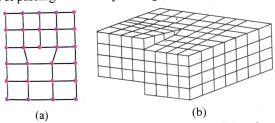


Fig. 1.77 (a) Edge dislocation and (b) screw dislocation

The screw dislocation [Fig. 1.77(b)] is so called because due to this defect, parallel atomic planes perpendicular to the axis are converted into a kind of helical ramp (during the formation of the crystal).

The linear defect or dislocation reduces the strength of the metal considerably. Even the chemical reactions that occur at the surface of the crystal tend to occur at the site of dislocations.

ILLUSTRATION 1.59

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If NaCl is doped with 10⁻² mol% SrCl₂, what is the concentration of the cation vacancies?

Sol. Doping of NaCl with 10⁻² mol % SrCl₂ means that 100 mol of NaCl are doped with 10^{-2} mol of SrCl₂.

 \therefore 1 mol of NaCl is doped with $SrCl_2 = \frac{10^{-2}}{100} = 10^{-4}$ mol

As each Sr2+ ion introduces one cation vacancy, therefore, the concentration of cation vacancies

= 10⁻⁴ mol/mol of NaCl

 $= 10^{-4} \times 6.023 \times 10^{23} \text{ mol}^{-1}$

 $= 6.02 \times 10^{19} \text{ mol}^{-1}$

ILLUSTRATION 1.60

If NaCl is doped with 10^{-3} mol% GaCl₃, what is the concentration of the cation vacancies?

Sol. 100 mol of NaCl are doped with 10⁻³ mol of GaCl₃.

$$\therefore \text{ 1 mol of NaCl is doped with } GaCl_3 = \frac{10^{-3}}{100} = 10^{-5} \text{ mol}$$

As one Ga^{3+} ion is introduced, three Na^{\oplus} have to be removed to maintain the electrical neutrality. So as one vacancy is filled by Ga3+, two cation vacancies are formed.

:. Concentration of cation vacancy

 $= 2 \times 10^{-5}$ mol/mol of NaCl

 $= 2 \times 10^{-5} \times 6.023 \times 10^{23} \text{ mol}^{-1}$

 $= 12.046 \times 10^{-18} \text{ mol}^{-1}$

 $= 1.2046 \times 10^{-19} \text{ mol}^{-1}$

ILLUSTRATION 1.61

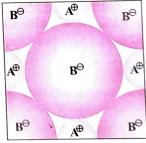
If all the atoms touching one face plane are removed in solid A[⊕]B[⊙] having rock salt type structure, then the formula of the compound left and the defect brought by this removal, respectively, is

a. AB, Frenkel defect

b. A2B, Frenkel defect

d. A₂B, Schottky defect c. AB, Schottky defect

Sol. c. i. Since A[⊕]B[⊙] has NaCl-type (fcc) structure. So B[⊙] are in fcc arrangement.



Removed atoms from one of the face

Number of B^{\odot} ions = 4

(Corner + face centre = 1 + 3 = 4)

Number of A^{\oplus} ions = 4

[in OV formed at body centre + edge centre = 1 + 3 = 4

Number of B[©] ions removed

= 4 corner $\times \frac{1}{6}$ per corner share

+ 1 face centre $\times \frac{1}{2}$ per face centre share

$$=\frac{4}{8}+\frac{1}{2}=1$$

Number of B^{Θ} left = 4 - 1 = 3

Number of A^{\oplus} ions removed

= 4 edge centre
$$\times \frac{1}{4}$$
 per edge centre share = $\frac{4}{4}$ = 1

Number of A^{\oplus} ions left = 4 - 1 = 3Thus, formula = $A_3B_3 = 3AB$.

ii. As atoms (or ions) are completely removed. Hence, the defect in the crystal is Schottky type.

ILLUSTRATION 1.62

The addition of CaCl, crystal to a KCl crystal

- a. Lowers the density of the KCl crystal
 - b. Raises the density of the KCl crystal
 - c. Does not affect the density of the KCl crystal
 - d. Increases the Frenkel defects of the KCl crystal

Sol. a. One Ca^{2^+} lets two K^{\oplus} leave the crystal to maintain the electrical neutrality of the compound.

The mass of two K^{\oplus} is greater than the mass of Ca^{2+} . Hence, density decreases.

ILLUSTRATION 1.63

What fraction of the surface of a crystal of Cd at T = 298 K consists of vacancies? Assume that the energy needed to form a vacancy = 0.5. For Cd(s), $\Delta_{\text{sub}}H^{\odot} = 112.0$ kJ mol⁻¹.

Sol. The number of vacancies (or Schottky defects) (n) is given by.

$$n = Ne^{-E/2KT}$$
 or $\frac{n}{N} = e^{-E/2KT}$

But fraction of the surface of a crystal vacancy is given by

$$\frac{n}{N} = e^{-E/RT}$$

$$= \exp\left[\frac{-(0.5)(112.0 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}\right] = 1.5 \times 10^{-10}$$

ILLUSTRATION 1.64

Calcium crystallizes in fcc unit cell with 0.556 nm. Calculate the density if

- a. It contains 0.2% Frenkel defects
- b. It contains 0.1% Schottky defects

Sol.

- a. Frenkel defects do not change the value of the theoretical density because the atom is occupying an interstitial position instead of a lattice position.
- **b.** Z_{eff} of Ca = 4 atoms/unit cell (since it is fee type) Since there are 0.1% Schottky defects,

So
$$Z_{\text{eff}} = \left(4 - \frac{0.1}{100} \times 4\right) = 3.996$$

$$\therefore \rho = \frac{Z_{\text{eff}} \times Aw}{N_{\text{A}} \times a^3} \ (\because 1 \text{ nm} = 10^{-9} \text{ m} = 10^{-7} \text{ cm})$$

$$= \frac{(3.996) \times 40 \text{ g}}{(6 \times 10^{23} \text{ mol}^{-1}) (0.556 \text{ nm} \times 10^{-7} \text{cm})^3}$$
$$= 1.547 \text{ g cm}^{-3}$$

1.27 ELECTRICAL PROPERTIES OF SOLIDS

Solids exhibit various range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^7 ohm m⁻¹. Solids are classified into three types on the basis of the conductivities.

- a. Conductors: The solids with conductivities rangin between 10⁴ and 10⁷ ohm⁻¹ m⁻¹ are called conductor Metals having conductivities in the order of 10⁷ ohm m⁻¹ are good conductors.
- **b. Insulators:** These are the solids with very low conductivities ranging between 10^{-20} and 10^{-10} ohm⁻¹ m⁻¹.
- c. Semiconductors: These are the solids with conductivities in the intermediate range from 10⁻⁶ to 10⁴ ohm⁻¹ m⁻¹.

1.27.1 CONDUCTION OF ELECTRICITY IN METALS

Metallic conductors conduct electricity through the movement electrons. Electrolytes conduct electricity through the movement of ions.

Metals conduct electricity in solid as well in as molten state. The conductivity of metals depends upon the number of valence electrons available per atom. The atomic orbitals of metal atom form molecular orbitals which are so close in energy to each other as to form a *band*. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal show conductivity [Fig. 1.78(a)].

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jumto it and such a substance has very small conductivity. It behave as an insulator [Fig. 1.78(b)].

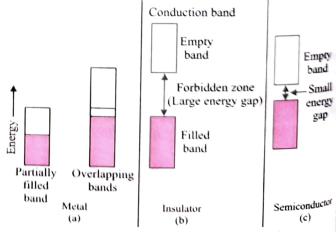


Fig. 1.78 Distinction among (a) metals, (b) insulators, and (c) semiconductors. In each case, an unshaded area represents a conduction basis

1.27.2 CONDUCTION OF ELECTRICITY IN SEMICONDUCTORS

In case of semiconductors, the gap between the valence band and In case of the conduction band is small [Fig. 1.78(c)]. Therefore, some electrons conduction band and show some conductivity. The may jump electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band, substances such as silicon and germanium show this type of behaviour and are called intrinsic semiconductors.

The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called doping. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce electronic defects in them.

1.27.3 ELECTRON-RICH IMPURITIES

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Si and Ge belong to Group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours [Fig. 1.79(a)]. When doped with a group 15 element such as P or As, which contains five valence electrons, they occupy some of the lattice sites in Si or Ge crystal [Fig. 1.79(b)]. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring Si atoms. The fifth electron is extra and becomes delocalized. These delegalized electrons increase the conductivity of doped Si (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called n-type semiconductor [Fig. 1.80(a)].

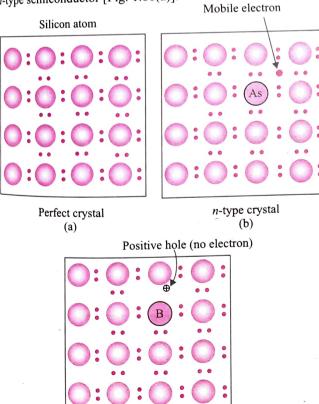


Fig. 1.79 Creation of n-type and p-type semiconductors by doping Group 13 and 15 elements

p-type crystal

1.27.4 ELECTRON-DEFICIT IMPURITIES

Si and Ge can also be doped with a group 13 element such as B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called electron hole or electron vacancy [Fig. 1.79(c)]. An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position.

If it happens it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semiconductors are called p-type semiconductors [Fig. 1.80(b)].

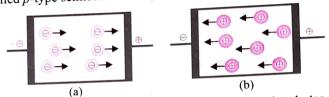


Fig. 1.80 (a) n-type semiconductor and (b) p-type semiconductor

1.27.5 APPLICATIONS OF N-TYPE AND P-TYPE SEMICONDUCTORS

Various combinations of n-type and p-type semiconductors are used for making electronic components. Diode is a combination of n-type and p-type semiconductors and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. npn and pnp type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for the conversion of light energy into electrical energy.

Ge and Si are Group 14 elements and, therefore, have a characteristic valency of 4 and form four bonds as in diamond. A large variety of solid state materials has been prepared by combination of Groups 13 and 15 or 12 and 16 to simulate average valency of 4 as in Ge or Si. Typical compounds of Groups 13-15 are InSb, AIP, and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionized the design of semiconductor devices. ZnS, CdS, CdSe, and HgTe are examples of Groups 12-16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

Transition metal oxides show marked differences in electrical properties. TiO, CrO₂, and ReO₃ behave like metals. Rhenium oxide, ReO₃, is like metallic copper in its conductivity and appearance. Certain other oxides such as VO, VO2, VO3, and TiO3 show metallic or insulating properties depending on temperature.

1.28 MAGNETIC PROPERTIES OF **SOLIDS**

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motion (a) its orbital motion around the nucleus and (b) its spin around its own axis (Fig. 1.81). Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton, μ_{B} . It is equal to $9.27 \times 10^{-24} \,\mathrm{A\,m}^2$.

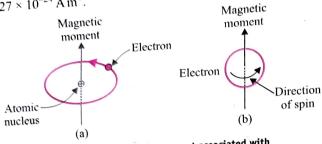


Fig. 1.81 The magnetic moment associated with (a) an orbiting electron and (b) a spinning electron

For each electron in an atom, the spin magnetic moment is $\pm \mu_B$ (depending upon two possibilities of the spin). The contribution of the orbital magnetic moment is equal to $m_l \mu_B$ where m_l is the magnetic quantum number of the electron.

Solids composed of atoms having completely filled electron shells or subshells are not capable of being permanently magnetized. This category includes the noble gases (such as He, Ne, Ar, etc.) as well as some ionic materials.

Solid materials are classified in different categories of magnetic materials based on the response of electron and atomic magnetic dipoles on application of an external applied magnetic field. Magnetic dipoles which may exist in a material can be considered analogous to electric dipoles. Magnetic dipoles may be thought of as small bar magnets composed of north and south poles instead of positive and negative electric charges. In our present discussion, magnetic dipole moment will be represented by arrows as shown in Figs. 1.82(a) and 1.82(b).

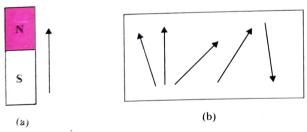


Fig. 1.82 (a) Magnetic moment as designated by an arrow and (b) in a paramagnetic substance

On the basis of their magnetic properties, substances can be classified into five categories: (a) paramagnetic (b) diamagnetic, (c) ferromagnetic, (d) antiferromagnetic, and (e) ferrimagnetic.

1.28.1 PARAMAGNETISM

Paramagnetic substances are weakly attracted by a magnetic field. They are magnetized in a magnetic field in the same direction and lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. For example, O₂, Cu²⁺, Fe³⁺, Cr³⁺.

1.28.2 DIAMAGNETISM

Diamagnetic substances are weakly repelled by magnetic field H_2O , NaCl, and C_6H_6 are some examples of such substances. The are weakly magnetized in a magnetic field in opposite direction Diamagnetism is shown by those substances in which all shows electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose the magnetic character.

1.28.3 FERROMAGNETISM

A few substances such as Fe, Co, Ni, Gd, and CrO2 are attracted very strongly by a magnetic field. Such substances are callferromagnetic substances. Besides strong attractions, the substances can be permanently magnetized. In solid state, metal ions of ferromagnetic substances are grouped together in small regions called domains. Thus, each domain acts as a tin magnet. In an unmagnetized piece of a ferromagnetic substant the domains are randomly oriented and their magnetic moment get cancelled. When the substance is placed in a magnetic field the domains get oriented in the direction of the magnetic field [Fi 1.83(a)] and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed at the ferromagnetic substance becomes a permanent magnet.

1.28.4 ANTIFERROMAGNETISM

Substances such as MnO showing anti-ferromagnetism har domain structure similar to ferromagnetic substance, but the domains are oppositely oriented and cancel out each other magnetic moment [Fig. 1.83(b)].

1.28.5 FERRIMAGNETISM

Ferrimagnetism is observed when the magnetic moments the domains in the substance are aligned in parallel and am parallel directions in unequal numbers [Fig.1.83(c)]. They a weakly attracted by magnetic field as compared to ferromagnet substances. Fe $_3$ O $_4$ (magnetite) and ferrites such as MgFe $_2$ O $_4$ ZnFe₂O₄ are examples of such substances. These substances als lose ferrimagnetism on heating and become paramagnetic.

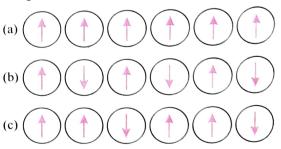


Fig. 1.83 Schematic alignment of magnetic moments in (a) ferromagnet (b) antiferromagnetic, and (c) ferrimagnetic substances

Note: All magnetically ordered solids (ferromagnetic antiferromagnetic, and ferrimagnetic solids) transform to the paramagnetic state at high temperature due to the randomization of spins. Ferrimagnetic material Fe₃O₄ becomes paramagneth at 850 K. It is also observed that ferromagnetic substances have a characteristic temperature above which no ferromagnetism observed. This is known as Curie temperature.

1.29 DIELECTRIC PROPERTIES OF SOLIDS

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In insulators, electrons are closely bound to individual atoms or ions and they do not generally migrate under an applied electric field. However, dipoles are created by a shift in charges, resulting in polarization. Besides that there may also be permanent dipoles in the crystal. Following situations may arise:

- a. These dipoles may align themselves in an ordered manner such that there is a net dipole moment in the crystal.
- b. These dipoles may align themselves in a manner such that dipole moments may cancel each other.
- c. There are no dipoles in the crystals, but only ions are present.

The crystals where situation (a) is found, exhibit *piezoelectricity* or pressure electricity. When such a crystal is deformed by mechanical stress electricity is produced due to the displacement of ion or if an electric field is applied to the crystal, there will be atomic displacement causing mechanical strain. The piezoelectric effect is demonstrated in Fig. 1.84.

Piezoelectric crystals are utilized in transducers devices, that convert electrical energy into mechanical strains or vice versa. Familiar applications that employ piezoelectrics include phonograph pickups, microphones, ultrasonic generators, strain gauges, and sonar detectors.

Piezoelectric materials include titanates of barium and lead, lead ziroconate (PbZrO₃), ammonium dihydrogen phosphate (NH₄H₂PO₄), and quartz. Some of the piezoelectric crystals when heated produce small electric potential or *pyroelectricity*.

In some of the piezoelectric crystals, the dipoles are permanently lined up (spontaneously polarized) even in the absence of an electric field, and the direction of polarization can be changed by applying an electric field. The phenomenon is called *ferroelectricity* by analogy with ferromagnetism.

Barium titanate (BaTiO₃), sodium potassium tartrate (Rochelle salt), and potassium dihydrogen phosphate (KH₂PO₄) are ferroelectric solids. If the dipoles align along alternate directions, there will be no net dipole moment and the crystal is said to be antiferroelectric. Lead zirconate (PbZrO₃) is a typical antiferroelectric solid.

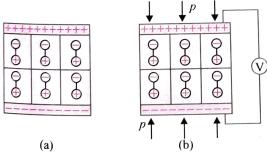


Fig. 1.84 (a) Dipoles within a piezoelectric material. (b) A voltage is generated when the material is subjected to a compressive stress (p)

1.29.1 SUMMARIZATION OF DIELECTRIC PROPERTIES OF POLAR CRYSTALS

Insulators do not conduct electricity because the electrons present in them are held tightly to the individual atoms or ions and are not

free to move. However when electric field is applied, polarization takes place because the nucleus is attracted toward cathode and electron cloud toward anode as shown in Fig. 1.85.

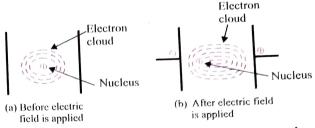


Fig. 1.85 These formed dipoles may align themselves in an ordered manner so that the crystal has a net dipole moment

Such polar crystals show following electrical properties:

- a. Piezoelectricity: When these crystals are subjected to mechanical stress, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. But if an electric field is applied to these crystals, there will be atomic displacement causing mechanical strain.
- **b. Pyroelectricity:** Some polar crystals when heated produce a small current or pyroelectricity.
- c. Ferroelectricity: In some piezoelectric crystals, the dipoles are permanently lined up even in the absence of an electric field. However, on applying electric field the direction of polarization changes, e.g., BaTiO₃, sodium potassium tartrate (Rochelle salt).

Note: All ferroelectric solids are piezoelectric, but the reverse is not true.

- d. Antiferroelectricity: If there is no net dipole moment it is said to be an antiferroelectric crystal. This is because the dipoles are alternately arranged. For example, lead zirconate (PbZrO₃).
- e. Superconductivity: When the electrical resistance of materials becomes almost zero, the material becomes superconductor. The temperature at which the material shows superconductivity is called *transition temperature*, e.g., YBa₂Cu₃O₇ at 90 K.

Table 1.14 Examples of some common magnetic and dielectric substance.

Type of substance		Examples
1.	Diamagnetic	N ₂ , NaCl, Zn, Cd, Cu [⊕] , TiO ₂
2.	Paramagnetic	Transition metals (Cr, Mn, Ni, Co Fe) metal ions (Cu ²⁺ , Ni ²⁺ , Fe ³⁺), metal oxides (CuO, VO ₂), molecules (NO and O ₂)
3.	Ferromagnetic	Ni, Fe, Co, CrO ₂
4.	Antiferromagnetic	MnO, Mn ₂ O ₃ , MnO ₂
5.	Ferrimagnetic	Fe ₃ O ₄ and pyrites
6.	Ferroelectric and piezoelectric	Rochelle salt (sodium potassium tartrate), KH ₂ PO ₄ , BaTiO ₃
7.	Antiferroelectric	PbZrO ₃ (lead zirconate)

CONCEPT APPLICATION EXERCISE 1.2

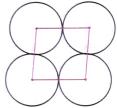
The number of Schottky defects (n) present in an ionic compound containing N ions at temperature T is given by n = Ne^{-E/2KT}, where E is the energy required to create n Schottky defects and K is the Boltzmann constant. If the mole fraction of Schottky defect in NaCl crystal at 2900 K is X, then calculate -ln(x).

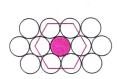
Given: ΔH of Schottky defect = 2 eV and

$$K = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$1 \text{ eV} = 1.608 \times 10^{-19} \text{ J}$$

- 2. FeO crystallizes in NaCl-type of crystal lattice. The crystals of FeO are deficient in iron and are always non-stoichiometric. Some cationic sites are vacant and some contain Fe³⁺ ions but the combination is such that the structure is electrically neutral. The formula approximates to Fe_{0.95}O.
 - **a.** What is the ratio of Fe^{2+} to Fe^{3+} ions in the solid?
 - b. What percentage of cation sites are vacant?
- 3. i. What is the relation between the radius of circle and the lenth of parallelogram for the unit cell shown in firgure below?





- ii. How many nearest neighbour circle does a given circle have in the second figure above?
- 4. i. Why is coordination number of 12 not found in ionic crystals?
 - ii. Out of NaCl and CsCl, which one is more stable and why?
- 5. How would you account for the following?
 - i. Frenkel defects are not found in alkali metal halides.
 - ii. Schottky defects lower the density of related solids.
- 6. a. What is levitation?
 - b. In what condition, mercury starts behaving as a superconductor?
- 7. The length of a unit cell in the nickel crystal is 0.352 nm. Diffraction of X-rays of 0.154 nm wavelength from a nickel crystal occurs at 22.2°, 25.9° and 38.2°. Show that these data are consistant with a face-centered cubic crystal structure.
- 8. Which oxide is used to make megnetic tapes? Which kind of magnetism is shown by this oxide?
- 9. If edge fraction unoccupied in ideal anti-fluorite structure
 - is X. Calculate the value of Z. Where $Z = \frac{X}{0.097}$
- Ionic solid Na[⊕]A[⊖] crystallise in rock salt type structure.
 2.592 gm of ionic solid salt NaA dissolved in water to make
 litre solution. The pH of this solution is 8. If distance between cation and anion is 300 pm, calculate density of ionic solid (in gm/cm³).

(Given:
$$pK_w = 13$$
, pK_a (HA) = 5, $N_A = 6 \times 10^{23}$)

- 11. Calculated the value of $\frac{Z}{20}$. Where
 - Z = Co-ordination number of 2D-square close packing

Co-ordination number of 2D-hcp

Co-ordination number of 3D-square close packing

Co-ordination number of 3D, ABCABC..... packing

Co-ordination number of 3D, ABAB..... packing

be placed such that their centres are laying in a square bound by four lines each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecule per unit area.

ANSWERS

1. $-\ln X \approx 4$

2. a. 8.5 **b.** 5%

9. 3

10. 4 g cm^{-3}

11. 2

12. 1.125

Solved Examples

EXAMPLE 1.1

The pyknometric density of NaCl crystal is 2.165×10^3 kg m⁻¹ while its X-ray density is 2.178×10^{-3} kg m⁻³. Calculate the fraction of unoccupied sites in NaCl crystal?

Sol. Molar volume from pyknometric density

Volume

$$= \frac{\text{Weight } (W)}{2.165 \times 10^3} \,\text{m}^3$$

Molar volume from X-ray density = $\frac{W}{2.178 \times 10^3}$ m³

Volume unoccupied =
$$\frac{W}{10^3} \left(\frac{1}{2.165} - \frac{1}{2.178} \right) \text{ m}^3$$

$$= \frac{0.013 W \times 10^{-3}}{2.165 \times 2.178}$$

:. Fraction unoccupied =
$$\left(\frac{0.013W \times 10^{-3}}{2.165 \times 2.178}\right) / \left(\frac{W \times 10^{-3}}{2.165}\right)$$

= 5.96×10^{-3}

EXAMPLE 1.2

The molar volumes of KCl and NaCl are 40 mL and 30 mL, respectively. Find the ratio of the unit cube edges of the two crystals. Assume both have the same packing efficiency.

Since both KCl and NaCl have fcc-type arrangement, therefore, Z_{eff} for both KCl and NaCl = 4/unit cell

Moreover, packing efficiency of both are same.

$$\frac{a_{\text{KCl}}^3}{a_{\text{NaCl}}^3} = \frac{\text{Volume of unit cell of KCl}}{\text{Volume of unit cell of NaCl}}$$

$$\therefore \frac{a_{\text{KCl}}}{a_{\text{NaCl}}} = \left(\frac{40}{30}\right)^{\frac{1}{3}} = 1.113$$

EXAMPLE 1.3

Calculate the void space in closest packing of n spheres of radius 1 unit, n spheres of radius 0.414 units, and 2n spheres of radius 0.225 units.

Sol. Since the packing is closest, therefore it is an fcc-type situation, $Z_{\text{eff}} = 4/\text{unit cell.}$ For fcc, $(4r)^2 = 2a^2$ (since r = 1 unit)

For fcc,
$$(4r)^2 = 2a^2$$
 (since $r = 1$ unit)

$$\therefore a = 2\sqrt{2}$$

Also, number of unit cell =
$$\frac{n}{4}$$

Volume of crystal =
$$\left(\frac{n}{4}\right) \times a^3 = \frac{n}{4} \times (2\sqrt{2})^3 = 4\sqrt{2}n$$

Volume of atoms =
$$\frac{n}{4} \begin{bmatrix} 4 \times \frac{4}{3} \pi (1)^3 + 4 \times \frac{4}{3} \pi (0.414)^3 \\ + 4 \times 2 \times \frac{4}{3} \pi (0.225)^3 \end{bmatrix} = 4.58n$$

$$\therefore$$
 Percentage of space occupied = $\frac{4.58n}{4\sqrt{2}n} \times 100 = 81\%$

Hence, void space = 100 - 81 = 19%

EXAMPLE 1.4

Calculate the following:

- Number of ZnS units in a unit cell of zinc blende.
- Number of CaF₂ units in a unit cell of CaF₂.

Sol. a.
$$Zn^{2+} = 4$$
 (within the body),

$$S^{2-} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$
(corners) (face centres)

b.
$$Ca^{2+} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

(corners) (face centres)
 $F^{\Theta} = 8$ (within the body)

EXAMPLE 1.5

If the length of the body diagonal for CsCl which crystallizes into a cubic structure with Cl[⊙] ions at the corners and Cs[⊕] ions at the centre of the unit cell is 7 Å and the radius of the Cs[®] ions is 1.69 Å, what is the radius of Cl[©] ions?

Sol. Length of the body diagonal = $2(r_{Cl} + r_{Cs})$

EXAMPLE 1.6

For a cubic crystal, the face diagonal is 3.50 Å. Calculate the

Sol. Face diagonal =
$$\sqrt{a^2 + a^2} = \sqrt{2}a$$

Face length $(a) = \frac{\text{Face diagonal}}{\sqrt{2}} = \frac{3.50\text{Å}}{\sqrt{2}} = \frac{3.50\text{Å}}{1.414}$
= 2.47Å

EXAMPLE 1.7

Cesium chloride forms a body-centred cubic lattice. Cesium and chloride ions are in contact along the body diagonal of a cell. The length of the side of the unit cell is 412 pm and Cl⁹ ion has a radius of 181 pm. Calculate the radius of Cs[®] ion.

Sol. Body diagonal =
$$\sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$$

= $2(r_{Cs} + r_{Cl})$
= $1.732 \times 412 \text{ pm}$
= 713.58 pm
 $\therefore r_{Cs} = \frac{713.58}{2} - r_{Cl}$
= $(356.79 - 181) \text{ pm}$
 $\approx 175.8 \text{ pm}$

EXAMPLE 1.8

A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?

Sol.
$$\rho = \frac{Z_{\text{eff}} \times Mw}{a^3 \times N_A \times 10^{-30}}$$
where a is in pm (1 nm = 10³ pm), Z_{eff} for NaCl = 4
$$= \frac{4 \times 58.5}{(0.564 \times 10^3)^3 \times (6.023 \times 10^{23}) \times 10^{-30}} \text{ g cm}^{-3}$$
= 2.165 g cm⁻³

EXAMPLE 1.9

In an Lil crystal, I ions form a cubical close-packed arrangement, and Li[®] ions occupy octahedral holes. What is the relationship between the edge length of the unit cells and radii of the I[□] ions? Calculate the limiting ionic radii of Li[⊕] and I[□] ions if a = 600 pm.

Sol. Cubical close packing implies that the unit cell of the I^{\odot} ion is fcc, and for that (from Table 1.12 and Fig. 1.59)

$$r_{\oplus} + r_{\odot} = a/2 = \frac{600}{2} = 300 \text{ pm}$$

For OV.

$$\frac{r_{\oplus}}{r_{\ominus}} = 0.414$$

$$r_{\odot} = 0.414 \times r_{\odot} = 0.414 \times 300 = 124.2 \text{ pm}$$

EXAMPLE 1.10

An element occurs in two crystalline forms α and β . The α -form has an fec with a=3.68 Å and β -form has a bcc with a=2.92 Å. Calculate the ratio of their densities.

Sol.
$$Z_{\text{eff}}$$
 for fec = 4, Z_{eff} for bcc = 2

Atomic volume of
$$\alpha$$
-form =
$$\frac{(3.68 \times 10^{-8})^3 \times N_A}{4}$$

Atomic volume of
$$\beta$$
-form = $\frac{(2.92 \times 10^{-8})^3 \times N_A}{2}$

(As Aw is same, element is same), so the density ratio is

$$\rho_{\alpha} : \rho_{\beta} = V_{\beta} : V_{\alpha} = \frac{(2.92)^3}{2} : \frac{(3.68)^3}{4}$$
$$= 12.448 : 12.459 = 1 : 1$$

EXAMPLE 1.11

Find the simplest formula of a solid containing A and B atoms in a cubic arrangement in which A occupies corner and B the centre of the faces of unit cell. If the side length is 5 Å, estimate the density of the solid assuming atomic weights of A and B as 60 and 90, respectively.

Sol. Simplest formula AB₃,
$$Mw = 60 + 3 \times 90 = 330$$

Volume of unit cell = $(5 \times 10^{-8})^3 = 125 \times 10^{-24}$ mL
One cell has one AB₃, molecule
So volume of one mole = $125 \times 10^{-24} \times 6.023 \times 10^{23}$
= 75.287 mL

Density =
$$\frac{330}{75.287}$$
 = 4.38 g cm⁻³

EXAMPLE 1.12

In the cubic crystal of CsCl (d = $3.97~g~cm^{-3}$), the eight corners are occupied by Cl $^{\odot}$ with a Cs $^{\oplus}$ at the centre and vice versa. Calculate the distance between the neighbouring Cs $^{\oplus}$ and Cl $^{\odot}$ ions. What is the radius of the two ions? (Aw of Cs = 132.91 and Cl = 35.45)

Sol. In a unit cell, there is one Cs[⊕] ion and one Cl[⊙] ion.

$$\rho = \frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}}$$

3.97 g cm⁻³ =
$$\frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}} \implies a = 4.13 \text{ Å}$$

For bcc.

$$2r_{\oplus} + 2r_{\odot} = \sqrt{3}a$$

$$r_{\oplus} + r_{\bigcirc} = \frac{\sqrt{3} \times 4.13}{2} = 3.57 \text{ Å}$$

 $2r_{\bigcirc} = 4.13 \text{ Å} \implies r_{\bigcirc} = 2.065$

$$r_{\oplus} = 3.57 - 2.065 = 1.505$$

Hence,
$$\frac{r_{\oplus}}{r_{\odot}} = 0.729$$
.

(The radius ratio suggests bcc structure)

EXAMPLE 1.13

Li forms a body-centred cubic lattice. If the edge of the cube is 3.5×10^{-10} m and the density is 5.3×10^2 kg m⁻³, calculate the percentage occupancy of Li metal.

Sol. Theoretical density

$$= \frac{Z_{\text{eff}} \times Aw}{N_{\text{A}} \times a^3} = \frac{2 \times 7 \times 10^{-3}}{6.023 \times 10^{23} \times (3.5 \times 10^{-10})^3}$$

$$= 5.4 \times 10^2 \text{ kg m}^{-3}$$

Percentage occupancy =
$$\frac{5.3 \times 10^2}{5.4 \times 10^2} \times 100 = 98\%$$

EXAMPLE 1.14

The metal ion—halide ion distances in several alkali metal halides are given. Explain only there is such a small difference in intenuclear distance between LiI and NaI compared to that between LiCl and NaCl.

Alkali	Distance, nm				
metal ion	\mathbf{I}^{\odot}	Cl [⊙]			
Li [⊕]	0.310	0.249			
Na [⊕]	0.317	0.279			
K [⊕]	0.352	0.314			
Rb [⊕]	0.367	0.329			

Sol. I^{\odot} ion and I^{\odot} ion contact in Li I makes closer approad impossible.

EXAMPLE 1.15

Calculate the ionic radius of F[⊙] ion.

2.19

Given: $r_1^{\odot} = 2.19 \text{ Å}$

and RbI =
$$3.67$$
 Å, RbBr = 3.44 Å, KBr = 3.29 Å,

$$KCl = 3.14 \text{ Å}, NaCl = 2.79 \text{ Å}, NaF = 2.31 \text{ Å}$$

Sol.

ıΘ

Argon crystallizes in fcc arrangement, and the density of solid and liquid Ar is 1.59 g cm⁻³ and 1.42 g cm⁻³, respectively. Find the percentage of empty space in liquid Ar.

Sol. First method

Let the volume of solid Ar = 100 mL

Mass of solid Ar = $V \times \rho = 100 \times 1.59 \text{ g cm}^{-3} = 159 \text{ g}$

Volume of liquid Ar = $\frac{\text{Mass}}{\rho} = \frac{159 \text{ g}}{1.42 \text{ g cm}^{-3}} = 112 \text{ mL}$

Since Ar crystallizes in fcc-type lattice, the packing fraction (PF) = 0.74

Actual volume occupied by $Ar = PF \times Volume of Solid Ar$ = $0.74 \times 100 = 74 \text{ mL}$

% Empty space in liquid Ar = $\frac{(112-74)\times100}{112}$ = 33.92%

Second method

Let the solid argon crystal = 100 g

Volume of Ar crystal (solid) = $\frac{100}{1.59}$ = mL

Volume of solid Ar in crystal = $PF \times Volume \text{ of Ar}$

crystal (solid)

$$= 0.74 \times \frac{100}{1.59} \, \text{mL}$$

Let the PF in liquid Ar in crystal = x

:. Volume of liquid Ar = Volume of solid Ar

PF × Volume of liquid Ar = $\frac{0.74 \times 100}{1.59}$ mL

$$x \times \frac{100}{1.42} = \frac{0.74 \times 100}{1.59} \implies x = 66.08\%$$

 $\therefore \text{ Empty space in liquid Ar} = 100 - 66.08$ = 33.92%

Third method

$$\frac{PF}{Density} = Constant$$

$$\frac{\text{PF(liquid Ar)}}{\rho \text{ of liquid Ar}} = \frac{\text{PF of solid Ar}}{\rho \text{ of solid Ar}}$$

$$\frac{x}{1.42} = \frac{0.74}{1.59} \Rightarrow x = 66.8\%$$

Empty space = 33.92%

EXAMPLE 1.17

The unit cell length of NaCl is 0.5 nm by X-ray diffraction method. The measured density of NaCl is 2.2 g cm⁻³. Correlate the difference of observed and calculated density and calculate the percentage of missing Na[®] and Cl[®] ions.

Sol. Since NaCl is an fcc-type arrangement,

$$\therefore Z_{\text{eff.}} \text{ of NaCl} = 4/\text{unit cell}$$

Mw of NaCl = 58.5; $(1 \text{ nm} = 10^{-9} \text{m} = 10^{-7} \text{cm})$

$$\therefore \rho_{\text{calculated}} = \frac{Z_{\text{eff}} \times Mw_{\text{(NaCl)}}}{N_{\text{A}} \times a^{3}}$$

$$= \frac{4 \times 58.5}{6 \times 10^{23} \times (0.5 \times 10^{-7})} \qquad ...(i)$$

$$= 3.12 \text{ g cm}^{-3}$$

Since $\rho_{observed} < \rho_{calculated}$, which implies that some of the sites are vacant.

$$\rho_{\text{obs}} = \frac{x \times 58.5}{6 \times 10^{23} \times (0.5 \times 10^{-7})^3} \text{ g cm}^{-3} \qquad ...(ii)$$

From equations (i) and (ii),

$$\rho_{\text{obs}} = x \frac{\rho_{\text{cal}}}{4} \Rightarrow \frac{\rho_{\text{obs}}}{\rho_{\text{cal}}} \times 4 = x$$

$$\Rightarrow \frac{2.2 \times 4}{3.12} = x$$

$$x = 2.82$$

Hence, missing sites = 4 - 2.82 = 1.18

% of missing sites = $\frac{1.18}{4} \times 100 = 29.5\%$

EXAMPLE 1.18

In an atomic fcc, all the lattice locations are occupied by A and the bode-centered OV is appropriately occupied by B, without disturbing the fcc of A. Calculate the packing fraction of this crystal.

Sol. For fcc arrangement,

Number of A atoms = 4

Number of B atoms = 1

Since it occupies only one body-centered OVs

For OV,
$$r_{\rm B} / r_{\rm A} = 0.414$$

$$a^3 = 16\sqrt{2}r_{\rm A}^2$$

$$PF = \frac{4 \times \frac{4}{3} \pi r_{A}^{3} + \frac{4}{3} \pi_{B}^{3}}{a^{3}}$$

$$= \frac{\pi}{3\sqrt{2}} \left[1 + \frac{1}{4} \left(\frac{r_{B}}{r_{A}} \right)^{3} \right]$$

$$= \frac{\pi}{3\sqrt{2}} \left[1 + \frac{1}{4} (0.414)^{3} \right]$$

$$= 0.74 \left[1 \times \frac{1}{4} (0.414)^{3} \right]$$

$$= 0.74 \left[1 + \frac{0.07}{4} \right]$$

$$= 0.74 \times 1.017 = 0.75$$

$$\therefore PF = 0.75$$

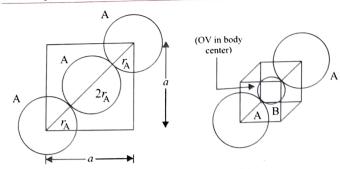


Fig. (a) Anion-anion (A-A) contact (b) Body-centered structure

$$(4r_A)^2 = 2a^2 \Rightarrow a = 2\sqrt{2} \ r_A \Rightarrow a^3 = 16\sqrt{2} \ r_A^3$$

A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, 1 g of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms.

(Aw of Ge = 72.6 and B = 11)

Sol. Assume here that the decrease in density is not due to volume change but due to loss of Ge atoms only. Let *x* be the total number of Ge atoms missing and *y* be the number of B atoms replacing Ge atoms. Assuming the volume of crystal remaining same, then 4% decrease in density will also decrease weight of the crystal (sample) by 4%.

$$\therefore 1 - \left(x \times \frac{72.6}{N_A}\right) + \left(y \times \frac{11}{N_A}\right) = 0.96$$

$$0.04 = \left(x \times \frac{72.6}{N_A}\right) - \left(y \times \frac{11}{N_A}\right)$$
where $y = \left(\frac{150N_A}{10^6 \times 11} \times 0.96\right)$

or
$$\frac{y \times 11}{N_A} = \frac{150 \times 0.96}{10^6}$$

$$0.04 = \left(x \times \frac{72.6}{N_{\rm A}}\right) - \left(\frac{150 \times 0.96}{10^6}\right)$$

$$\therefore x = \frac{(0.04 + 1.44 \times 10^{-4})N_A}{72.6} \approx \frac{0.04N_A}{72.6}$$

$$\therefore \frac{y}{x} = \frac{150N_{A} \times 0.96 \times 72.6}{10^{6} \times 11 \times 0.04N_{A}} = 2.376 \times 10^{-2}$$

$$\therefore \frac{y}{x} \times 100 = 2.376 \times 10^{-2} \times 100$$
$$= 2.376\%$$

EXAMPLE 1.20

A tetrahedron can be drawn within a cube. The center of the cube constitutes a tetrahedral void. In closest packing, two anion touch each other along the face diagonal of the cube and on cation (occupying a tetrahedral void) and two anions (occupying two remote corners) touch each other along the cross diagonal of the cube. Using these facts, show that $r_{\oplus}/r_{\odot} = 0.225$.

Sol. Face diagonal of cube = $\sqrt{2}a$

Cross diagonal of cube = $\sqrt{3}a$

Hence,
$$2r_{\odot} = \sqrt{2}a$$

$$2r_{\oplus} + 2r_{\odot} = \sqrt{3}a$$

Divinding equations (i) and (ii),

$$\frac{2r_{\oplus} + 2r_{\odot}}{2r_{\odot}} = \frac{\sqrt{3}a}{\sqrt{2}a}$$

$$\frac{r_{\oplus}}{r_{\odot}} = \frac{\sqrt{3}}{2} - 1 = 0.225$$

EXAMPLE 1.21

An octahedron can be drawn within a cube by choosing the centers of its six faces. The center of the cube constitutes at octahedral void. In closest packing, two anions touch each other along the line obtained by joining the centers of two adjoining faces and one cation (occupying an octahedral void) and two anions (occupying centers of two opposite faces) touch each other along the line joining the centers of two opposite faces. Using these facts, show that $r_{\oplus} / r_{\odot} = 0.414$.

Sol. Distance between the center of two adjoining faces = $\frac{a}{\sqrt{1}}$

Distance between the center of two opposite faces = a

Hence,
$$2r_{\odot} = \frac{a}{\sqrt{2}}$$

and
$$2r_{\oplus} + 2r_{\odot} = a$$

On dividing,

$$\frac{2r_{\oplus} + 2r_{\odot}}{2r_{\odot}} = \frac{a}{a/\sqrt{2}}$$

$$\frac{r_{\oplus}}{r_{\odot}} = \sqrt{2} - 1 = 0.414$$

EXAMPLE 1.22

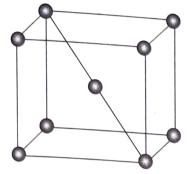
Potassium crystallizes in a body-centered lattice with a u^{a} cell (a) = 5.20 Å.

- a. What is the distance between the nearest neighbours
- b. What is the distance between the next-nearest neighbours?
- c. How many nearest neighbours does K atom have?
- d. What is the calculated density of crystalline K?

Sol.

a. The body diagonal is $\sqrt{3}a = \sqrt{3} (5.20 \text{ Å}) = 9.01 \text{ Å}$ The nearest neighbours along the diagonal are half the distance apart, 4.50 Å.

- 5.20 Å, along the cell edge. b.
- 8 (For example, the body center is next to 8 corners). c.
- 6 (The corner has neighbours along each cell edge, up, d. down, in, out, left, right).
- Two K atoms per unit cell; one at the body center and e. one-eighth at each corner.



$$\rho = \frac{Z_{\text{eff}} \times Aw}{a^3 \times N_A}$$

$$\therefore \rho \times a^3 = \frac{Z_{\text{eff}} \times Aw}{N_A} (Z_{\text{eff}} \text{ for bcc} = 2)$$

$$\text{Mass} = \frac{Z_{\text{eff}} \times Aw}{N_A}$$

$$= 2\left(\frac{39.1 \text{ g}}{6.02 \times 10^{23}}\right) = 1.30 \times 10^{-22} \text{ g}$$

Volume =
$$a^3$$

= $\left[(5.20 \text{ Å}) \left(\frac{10^{-8} \text{ cm}}{1 \text{ Å}} \right) \right]^3$
= $1.41 \times 10^{-22} \text{ cm}^3$

$$\rho = \left(\frac{\text{Mass}}{\text{Volume}} \right) = \frac{1.30 \times 10^{-22} \text{ g}}{1.41 \times 10^{-22} \text{ cm}^3} = 0.925 \text{ g cm}^{-3}$$

Lithium metal has a body-centered cubic unit cell.

- a. How many atoms are there in a unit cell?
- b. Krypton crystallizes in a structure that has four Kr atoms in each unit cell and the unit cell is a cube. The edge length of the unit cell is 0.558 nm. Calculate the density of crystalline Kr in kg m⁻³.

a. Two (one at the corners, equivalent to 1/8th at each of eight corners, plus one at the body center).

eight corners, plus one at the body center).
b. Mass =
$$(4 \text{ atoms}) \left(\frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} \right)$$

$$\left(\frac{83.8 \times 10^{-3} \text{ kg}}{\text{mol}} \right)$$
= $5.57 \times 10^{-25} \text{ kg}$
Volume = $(0.558 \times 10^{-9} \text{ m})^3 = 1.75 \times 10^{-28} \text{ m}^3$

$$\rho = \frac{M}{V} = \frac{5.57 \times 10^{-25} \text{ kg}}{1.75 \times 10^{-28} \text{ m}^3} = 3190 \text{ kg m}^{-3}$$

EXAMPLE 1.24

Iron crystallizes in several modifications. At about 910°C, the bcc α -form undergoes a transition to the face-centered cubic γ-form. Assuming that the distance between nearest neighbours is the same in the two forms at the transition temperature. Calculate the ratio of the density of iron of fcc form to that of iron of bcc form at the transition temperature.

Sol. For α -form, distance between nearest neighbour is $\sqrt{3}a_1/2$ (For bcc, $Z_{\text{eff}} = 2/\text{unit cell}$)

For γ -form, distance between nearest neighbour is $a_2/\sqrt{2}$ (For fcc, $Z_{\rm eff} = 4/{\rm unit}$ cell)

As the distance between nearest neighbours is same in the

$$\therefore \frac{\sqrt{3}a_1}{2} = \frac{a_2}{\sqrt{2}}$$

$$\frac{a_2}{a_1} = \sqrt{\frac{3}{2}}$$

$$\left[\text{since } \frac{Z_{\text{eff(bcc)}}}{Z_{\text{eff(fcc)}}} = \frac{2}{4} = \frac{1}{2}\right]$$

$$\frac{\rho_1}{\rho_2} = \frac{(Z_{\text{eff}})_1}{(Z_{\text{eff}})_2} \left(\frac{a_2}{a_1}\right)^3 = \frac{1}{2} \left(\sqrt{\frac{3}{2}}\right)^2 = 0.918$$

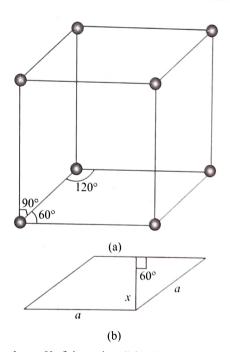
where ρ_1 is the density for $\alpha\text{-form}$ and ρ_2 is the density for

EXAMPLE 1.25

Ice crystallizes in a hexagonal lattice. At low temperature at which the structure was determined, the lattice constants are: a = 4.53 Å, and c (height) = 7.41 Å.

How many H₂O molecules are contained in a unit cell? (Density of ice = 0.92 g cm^{-3}).

Sol.

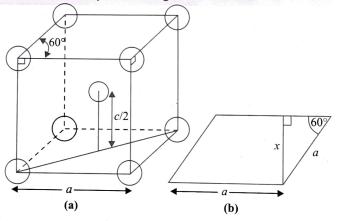


The volume V of the unit cell in Fig. (a) and (b): V =Area of rhombus base \times Height (c) $= (a^2 \sin 60^\circ) \times c = (4.53 \text{ Å})^2 (0.866) (7.41 \text{ Å})$

- 132 Å³ = 132 × 10⁻²⁴ cm³
Mass of unit cell =
$$V \times$$
 Density
= (132 × 10⁻²⁴ cm³) (0.92 g cm⁻³) × (6.02 × 10²³)
= 73 g
Number of moles of H₂O = $\frac{73}{18} \approx 4$

A hexagonal close-packed lattice can be represented by figures (a) and (b) below. If $c = a\sqrt{\frac{8}{3}} = 1.633a$, there is an atom at each corner of the unit cell and another atom which can be located by moving one-third the distance along the dioagonal of the rhombus base, starting at the lower left hand corner and moving perpendicularly upward by c/2. Mg crystallizes in this lattice and has a density of $1.74 \, \mathrm{g \, cm}^{-3}$.

- a. What is the volume of unit cell?
- b. What is a?
- c. What is the distance between nearest neighbours?
- d. How many nearest neighbours does each atom have?



Sol.

a.
$$Z_{\text{eff}} = 8 \text{ (corners)} \times \frac{1}{8} \text{ (per corner share)}$$

= 2 atoms/unit cell

$$Aw$$
 of Mg = 24.3 g

Mass = (2 atoms)
$$\left(\frac{24.3 \text{ g}}{6.02 \times 10^{23} \text{ atoms}}\right) = 8.07 \times 10^{-23} \text{ g}$$

Volume = $\frac{\text{Mass}}{\text{Density}} = \left(\frac{8.07 \times 10^{-23} \text{ g}}{1.74 \text{ g cm}^{-3}}\right) \times (10^8 \text{ Å})^3$

$$=46.4$$
Å

b. The base area of the cell [Fig. (b)] is:

$$\sin 60^\circ = \frac{x}{a} \Rightarrow x = a(\sin 60^\circ) = a(0.8660)$$

 $\therefore \text{ Area} = ax = 0.8660a^2$

Volume = Area × Height
=
$$(0.8660a^2) (1.633a) = 1.414a^3 = 46.4 \text{ Å}^3$$

Thus, $a = 3.20 \text{ Å}$

- c. Distance between nearest neighbours = 3.20 Å Nearest neighbours are along the base edge.
- d. 12 neighbours atoms. The 12 atoms are most easy viewed as six atoms in the same plane, three above at three below.

The plane of the six atoms around the central atom $i_{\delta, \eta}$ shown in the above figure.

EXAMPLE 1.27

Titanium (Ti) crystallizes in fcc lattice. It reacts with C or interstitially and these elements occupy the voids of host lattic (i.e., Ti). H-atom occupies TVs but C-atom occupies OVs

- a. Calculate the formula of titanium hydride and titanium carbide.
- b. What is the maximum ratio of "foreign" atom radiu (i.e., H atom) to host atom (i.e., Ti) radius that can be occupied in TVs without causing a strain in the host lattice.
- c. What is the maximum allowable radius ratio in an 00
- d. Account for the fact that H-atom occupy TVs while C-atoms occupy OVs.

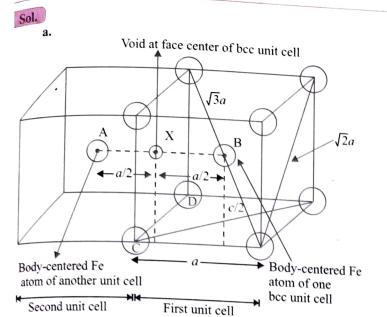
Sol.

- a. For fcc lattice, $Z_{\rm eff}$ = 4 Ti atoms/unit cell Number of TVs = Number of H-atoms = 8/unit cell
 - i. Formula of titanium hydride = $Ti_4H_8 \Rightarrow TiH_2$
 - ii. Number of OVs = Number of C-atom = 4/unit celFormula of titanium carbide = $\text{Ti}_4\text{C}_4 \Rightarrow \text{TiC}$
 - **b.** For TVs, $\frac{r_{\oplus}}{r_{\odot}} = \frac{r_{\text{H}}}{r_{\text{Ti}}} = 0.225$
 - **c.** For OVs, $\frac{r_{\oplus}}{r_{\odot}} = \frac{r_{\text{C}}}{r_{\text{Ti}}} = 0.414$
 - **d.** Size of H-atom is small in comparision of C-atom, H occupies TVs and C occupies OVs.

EXAMPLE 1.28

Iron cryatallizes in two bcc lattices, the α -form below 910° and the δ -form above 1400°C, and in an fcc γ -atom between these two temperatures.

- a. What is the symmetry of a face-centered void of a but unit cell?
- b. What is the maximum symmetry of a void whose coordinates are (0, a/2, a/4) is bcc unit cell?
- c. What is the maximum ratio of a foreign particle radio occupying such a void to the host iron ion radius?
- d. Why does only the γ-form dissolve appreciable amount of carbon?



In bcc, the atom at the body center B is in contact with those at the corners; the corner atoms do not touch each other.

The body diagonal = $\sqrt{3}a = 4r$

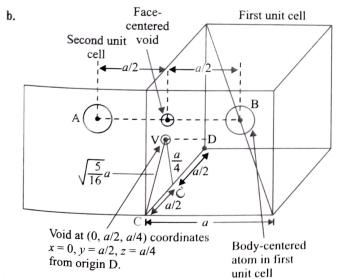
Thus,
$$a = \left(\frac{4}{\sqrt{3}}\right)r$$
 ...(i)

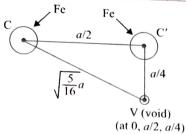
From body center to body center (A - B) = a (figure above)

Also,
$$a = 2r_{(Fe)} + 2r_{(void)} = \frac{4r}{\sqrt{3}}$$

$$\therefore r_{\text{Fe}} + r_{\text{void}} = \frac{2}{\sqrt{3}}r, \quad \therefore \quad \frac{r_{\text{void}}}{r_{\text{Fe}}} = \left(\frac{2}{\sqrt{3}} - 1\right) = 0.155$$

The face diagonals are longer $(\sqrt{2}a)$ than the distance between body centers, so the geometry of the void is a shortened octagedron called distorted octahedral.





Consider the body-centered atoms (A and B) and the two corners atoms at the base of the face joining two unit cell (C and D) (figure above).

The distance from the center of the line joining the top atom to that joining the bottom atom = a/2.

(The bottom atoms are a half unit cell below the top ones). The void (V) is located half way down the line, as required by symmetry. The triangle (VCC') has one side a/2 and one

side is a/4. The hypotenuse (VC) = $\sqrt{\frac{5}{16}} a$.

$$\therefore r_{\text{Fe}} + r_{\text{V}} = \sqrt{\frac{5}{16}} \ a = \sqrt{\frac{5}{16}} \left(\frac{4r}{\sqrt{3}}\right) = \sqrt{\frac{5}{3}}r$$

$$\therefore r_{\rm V} = \left(\sqrt{\frac{5}{3}} - 1\right) r_{\rm Fe.}$$

c.
$$\frac{r_{\rm V}}{r_{\rm Fe}} = \left(\sqrt{\frac{5}{3}} - 1\right) = 0.291$$

d. Carbon is too big to occupy either type of void in a bcc structure but can fit with in an OV of an fcc structure. (i.e., γ -form)

EXAMPLE 1.29

Argon crystallizes in a structure in which the atoms are located at the positions (0,0,0), $\left(0,\frac{1}{2},\frac{1}{2}\right)$, $\left(\frac{1}{2},0,\frac{1}{2}\right)$, and $\left(\frac{1}{2},\frac{1}{2},0\right)$. The unit cell is

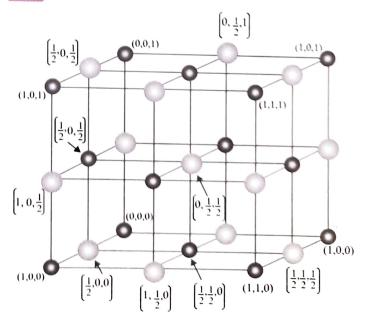
a. sc

b. bee

c. fcc

d. dc

Sol. c.



The ratio of the volume of a tetragonal lattice to that of hexagonal

a.
$$\frac{2}{\sqrt{3}}$$

a.
$$\frac{2}{\sqrt{3}}$$
 b. $\frac{\sqrt{3}}{2} abc$ c. $\frac{\sqrt{3}a^2}{2bc}$ d. $\frac{2a^2c}{\sqrt{3}b}$

d.
$$\frac{2a^2c}{\sqrt{3}b}$$

Sol. a. Volume of a lattice is given by:

$$V = abc \left(\frac{1 - \cos^2 \pm - \cos^2 2 - \cos^2 3}{-2\cos\alpha\cos\beta\cos\gamma} \right)^{\frac{1}{2}}$$

$$V_{\text{tetragonal}} = a^2 c \text{ (because } a = b \neq c, \alpha = \beta = \gamma = 90^{\circ})$$

$$V_{\text{hexagonal}} = a^2 c \times \frac{\sqrt{3}}{2} \qquad \begin{cases} \text{because } a = b \neq c, \\ \alpha = \beta = 90^{\circ}, \\ \gamma = 120^{\circ} \end{cases}$$

$$\therefore \frac{V_{\text{tetragonal}}}{V_{\text{hexagonal}}} = \frac{a^2c \times 2}{\sqrt{3} \times a^2c} = \frac{2}{\sqrt{3}}$$

Exercises

Single Correct Answer Type

Classification of Solids and Their Properties

- 1. Which one is called pseudo solid?
 - (1) CaF,
- (2) Glass
- (3) NaCl

- (4) All
- 2. Solids which do not show the same physical properties in different direction are called:
 - (1) Pseudo solids
- (2) Isotropic solids
- (3) Polymorphic solids
- (4) Anisotropic solids
- 3. Graphite is an example of:
 - (1) Ionic solid
- (2) Covalent solid
- (3) Metallic crystal
- (4) None of these
- 4. Amorphous solids are:
 - (1) Isotropic and supercooled liquids
 - (2) Anisotropic and supercooled liquids
 - (3) Isoenthalpic and superheated liquids
 - (4) Isotropic and superheated solids
- 5. Crystals which are good conductor of electricity and heat
 - (1) Ionic crystals
- (2) Covalent crystals
- (3) Metallic crystals
- (4) Molecular crystals
- 6. Which of the crystal systems contains the maximum number of Bravais lattices?
 - (1) Cubic
- (2) Hexagonal
- (3) Triclinic
- (4) Orthorhombic
- 7. The most unsymmetrical and symmetrical systems are, respectively:
 - (1) Tetragonal, Cubic
 - (2) Triclinic, Cubic
 - (3) Rhombohedral, Hexagonal
 - (4) Orthorhombic, Cubic
- 8. The crystal system of a compound with unit cell parameters, a = 0.328 nm, b = 0.328 nm, c = 0.527 nm and $\alpha = \beta = \gamma =$ 90° is
 - (1) Cubic
- (2) Tetragonal
- (3) Monoclinic
- (4) Rhombohedral
- 9. What are the number of atoms per unit cell and the number of nearest neighbours in a simple cubic structures?
 - (1) 1, 6

(2) 4, 12

(3) 2, 8

- (4) 2, 6
- 10. What are the number of atoms per unit cell and the number of nearest neighbours in a face centered cubic structures?
 - (1)4,8

(2) 2, 8

(3) 2, 6

- (4) 4, 12
- 11. What are the number of atoms per unit cell and the number of nearest neighbours in a body centered cubic structurers?
 - (1) 4, 12
- (2) 1, 6

(3) 2, 8

(4) 2, 5

- 12. Which of the following layering pattern will have a void
 - (1) ABCCBAABC
- (2) ABBAABBA
- (3) ABCABCABC
- (4) ABCAABCA
- 13. If the ratio of coordination no. of A to that of B is x : y, then the ratio of no. of atoms of A to that no. of atoms of B in unit cell is:
 - (1) x : v
- (3) $x^2 : v$
- 14. When heated above 916°C, iron changes its bcc crystalline form to fcc without the change in the radius of atom. The ratio of density of the crystal before heating and after heating
 - (1) 1.069
- (2)0.918
- (3) 0.725
- (4) 1.231
- 15. TIAI(SO₄)₂. xH_2O is bcc with 'a' = 1.22 nm. If the density of the solid is 2.32 g/cc, then the value of x is (Given: $N_A =$ 6×10^{23} ; at. mass: TI = 204, AI = 27, S = 32).
 - (1)2

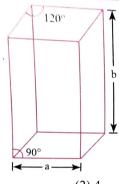
(2)4

(3)47

- (4)70
- 16. A body centered cubic lattice is made up of hollow spheres of B. Spheres of solid A are present in hollow spheres of B. Radius of A is half of radius of B. What is the ratio of total volume of spheres of B unoccupied by A in a unit cell and volume of unit cell?
 - (1) $\frac{7\sqrt{3\pi}}{64}$
- (2) $\frac{7\sqrt{3}}{128}$

(3) $\frac{7\pi}{24}$

- (4) $\frac{7\pi\sqrt{3}}{64}$
- 17. First three nearest neighbour distances for primitive cubic lattice are respectivly (edge length of unit cell = a):
 - (1) $a, \sqrt{2a}, \sqrt{3a}$
- (2) $\sqrt{3}a$, $\sqrt{2}a$, a
- (3) $a, \sqrt{2a}, 2a$
- (4) $a, \sqrt{3}a, 2a$
- 18. First three nearest neighbour distances for body centered cubic lattice are respectively:
 - $(1)\sqrt{2a}$, a, $\sqrt{3a}$
- (2) $\frac{a}{\sqrt{2}}$, a, $\sqrt{3}a$
- (3) $\frac{\sqrt{3}a}{2}$, a, $\sqrt{2}a$
- (4) $\frac{\sqrt{3}a}{2}$, a, $\sqrt{3}a$
- 19. In a planar tetra-atomic molecule, XY_3 , X is at the centroid of the equilateral tringle formed by the atoms, Y. If the X-Ybond distance is 1 Å, what is the distance between the centres of any two Y atoms?
 - (1) $1/\sqrt{3}$ Å
- (2) $\sqrt{2} \text{ Å}$
- (3) $\sqrt{3} \text{ Å}$
- (4) $1/\sqrt{2}$ Å
- **20** A_2B molecules (molar mass = 259.8 g/mol) crystallises in a hexagonal lattice as shown in figure. The lattice constants are a = 5 Å and b = 8 Å. If density of crystal is 5 g/cm³ then how many molecules are contained in given unit cell? (use $N_{\Lambda} = 6 \times 10^{23}$



(1) 6

(2)4

(3)4

- (4) 2
- 21. Graphite has h.c.p arrangements of carbon atoms and the parallel planes are 3.55 Å apart. Determine density of graphite:
 - (1) 2.46 g/cc
- (2) 0.41 g/cc
- (3) 1 g/cc
- (4) 1.41 g/cc
- **22.** Select right experssion for determining packing fraction (P.F.) of NaCl unit cell (assume ideal) if ions along an edge diagonal are absent:

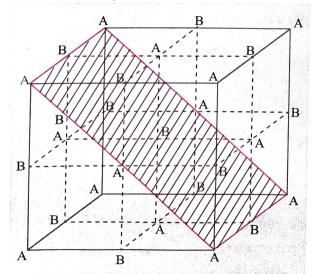
(Given: volume of unit cell = $16\sqrt{2} r_{\odot}^3$)

(1) P.F. =
$$\frac{\frac{4}{3}\pi (r_{\oplus}^3 + r_{\odot}^3)}{16\sqrt{2} r_{\odot}^3}$$
 (2) P.F. = $\frac{\frac{4}{3}\pi \left(\frac{5}{2}r_{\oplus}^3 + 4r_{\odot}^3\right)}{16\sqrt{2} r_{\odot}^3}$

(3) P.F. =
$$\frac{\frac{4}{3}\pi\left(\frac{5}{2}r_{\oplus}^3 + r_{\odot}^3\right)}{16\sqrt{2}r_{\odot}^3}$$
 (4) P.F. = $\frac{\frac{4}{3}\pi\left(\frac{7}{2}r_{\oplus}^3 + r_{\odot}^3\right)}{16\sqrt{2}r_{\odot}^3}$

- **23.** A crystal is made of particles *X*, *Y* and *Z*. *X* forms fcc packing. *Y* occupies all the octahedral voids of *X* and *Z* occupies all the tetrahedral voids of *X*. If all the particles along one body diagonal are removed then the formula of the crystal would be:
 - $(1) XYZ_2$

- $(2) X_2 Y Z_2$
- $(3) X_{8} Y_{4} Z_{5}$
- $(4) X_5 Y_4 Z_8$
- **24.** A crystal is made of particles *A* and *B*. A forms fcc packing and *B* occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then, the formula of the crystal would be:

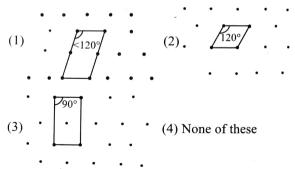


(1) AB

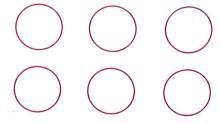
 $(2) A_5 B_7$

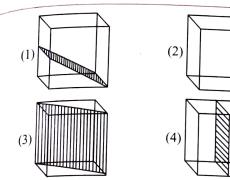
 $(3) A_7 B_5$

- (4) None of these
- 25. Given length of side of hexagonal unit cell is $\frac{100}{\sqrt{2}}$ pm. The volume of hexagonal unit cell is (in pm³):
 - $(1) 8 \times 10^6$
- (2) 1.5×10^6
- $(3) 64 \times 10^6$
- $(4)\ 36 \times 10^6$
- **26.** A crystal may have one or more planes and one or more $a_{X_{\xi_1}}$ of symmetry but it possesses:
 - (1) Two centres of symmetry
 - (2) One centre of symmetry
 - (3) No centre of symmetry
 - (4) None of the above
- 27. TiO₂ is well known example of:
 - (1) Triclinic system
- (2) Tetragonal system
- (3) Monoclinic system
- (4) None of these
- 28. The crystals are bounded by plane faces (f), straight edges (e) and interfacial angle (c). The relationship between these is:
 - (1) f + c = e + 2
- (2) f + e = c + 2
- (3) c + e = f + 2
- (4) None of these
- 29. Ice molecules can exhibit up to sixteen different phases that depend on temperature and pressure. Which of the following diagram represents the location of lattice points within the space lattice of ice



- 30. Liquid H₂O is densest, essentially 1.00 g/cm³, at 4°C and becomes less dense as the water molecules begin to form crystals ice as the freezing point is reached. Ice is 83 % less dense then liquid water the structure of ice is:
 - (1) Cubic
- (2) Hexagonal
- (3) Orthorhombic
- (4) Rhombohedral
- 31. Which of the following shaded plane in fcc lattice contains arrangement of atoms as shown below:

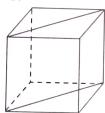




- 32. A metal crystallises in bcc lattice. The % fraction of edge length not covered by atom is:
 - (1) 10.24 %
- (2) 13.4%
- (3) 12.4 %

 e_s

- (4) 11.4%
- 33. A crystal is made up of particles X, Y, and Z. X forms fcc packing. Y occupies all octahedral voids of X and Z occupies all tetrahedral voids of X. If all the particles along one body diagonal are removed, then the formula of the crystal would be
 - (1) XYZ₂
- (2) X₂YZ₂
- $(3) X_{8} Y_{4} Z_{5}$
- $(4) X_5 Y_4 Z_8$
- 34. In a hypothetical solid, C atoms are found to form cubical close-packed lattice. A atoms occupy all tetrahedral voids and B atoms occupy all octahedral voids.



A and B atoms are of appropriate size, so that there is no distortion in the ccp lattice of C atoms. Now if a plane as shown in the following figure is cut, then the cross section of this plane will look like







35. What is the maximum number of layers of atoms in closepacked planes that will lie within two imaginary parallel

planes having a distance between them of $13\sqrt{\frac{2}{3}}r$ (where

r is the radius of atom) in the copper crystal (fcc)?

(Consider the atoms to be within the parallel planes if their centres are on or within the two parallel planes).

(1)5

(2)6

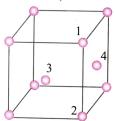
(3)7

(4) 8

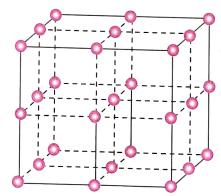
- 36. Analysis show that nickel oxide consists of nickel ion with 96% ions having d⁸ configuration and 4% having d⁷ configuration. Which amongst the following best represents the formula of the oxide?
 - (1) $Ni_{1.02}O_{1.00}$
- (2) $Ni_{0.96}O_{1.00}$
- $(3) Ni_{0.98}O_{0.98}$
- (4) Ni_{0.98}O_{1.00}
- 37. What is the density of Na₂O having antifluorite-type crystal structure, if the edge length of cube is 100 pm and what is the effect on density by 0.05% Frenkel defect?

 - (1) 823.5 g cm⁻³, density decreases (2) 414.16 g cm⁻³, density decreases

 - (3) 823.5 g cm⁻³, density remains same (4) 414.16 g cm⁻³, density remains same
- 38. In the calcium fluoride structure, the coordination number of the cations and the anions are, respectively,
 - (1) 6 and 6
- (2) 8 and 4
- (3) 4 and 4
- (4) 4 and 8
- 39. A metallic crystal crystallizes into a lattice containing a sequence of layers ABABAB... . Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space?
 - (1) 74%
- (2) 26%
- (3)50%
- (4) None of these
- 40. In an fcc unit cell, atoms are numbered as shown below. The atoms not touching each other are (Atom numbered 3 is face centre of front face)



- (1) 3 and 4
- (2) 1 and 3
- (3) 1 and 2
- (4) 2 and 4
- 41. The number of nearest neighbours and next nearest neighbours of an Na[⊕] ion in a crystal of NaCl are, respectively,
- (2) 6Cl[⊙], 12Na[⊕]
- (1) 6Na[⊕], 12Cl[⊙] (3) 12Cl[⊙], 12Na[⊕]
- (4) 6Cl[©], 6Na[⊕]
- 42. The following diagram shows the arrangement of lattice points with a = b = c and $\alpha = \beta = \gamma = 90^{\circ}$. Choose the correct options.



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- (1) The arrangement is sc with each lattice point surrounded by 6 nearest neighbours.
- (2) The arrangement is sc with each lattice point surrounded by 8 nearest neighbours.
- (3) The arrangement is fcc with each lattice point surrounded by 12 nearest neighbours.
- (4) The arrangement is bcc with each lattice point surrounded by 8 nearest neighbours.
- **43.** The number of atoms in 100 g of an fcc crystal with density $= 10.0 \text{ g cm}^{-3}$ and cell edge equal to 200 pm is equal to

$$(1) 5 \times 10^{24}$$

(2)
$$5 \times 10^{25}$$

$$(3) 6 \times 10^{23}$$

(4)
$$2 \times 10^{25}$$

(1)
$$a = b = c$$
, $\alpha = \beta = 90^{\circ} \neq \gamma$

(2)
$$\alpha = \beta = \gamma = 90^{\circ}$$
, $a = b \neq c$

(3)
$$\alpha = \beta = \gamma = 90^{\circ}$$
, $a \neq b \neq c$

(4)
$$\alpha = \beta = 90^{\circ}, \gamma = 120^{0}, a = b \neq c$$

- **45.** If the lattice parameter of Si = 5.43 Å and the mass of Si atom is $28.08 \times 1.66 \times 10^{-27}$ kg, the density of silicon in kg m⁻³ is (Given: Silicon has diamond cubic structure)
 - (1) 2330

- (3) 3445
- (4) 1673
- **46.** The lattice parameter of GaAs (radius of Ga = 1.22 Å,

$$As = 1.25 \text{ Å}) \text{ is}$$

- (1) 5.635 Å
- (2) 2.852 Å
- (3) 5.774 Å
- (4) 4.94 Å
- **47.** In cubic ZnS (II–VI) compounds, if the radii of Zn and S atoms are 0.74 Å and 1.70 Å, the lattice parameter of cubic ZnS is
 - (1) 11.87 Å
- (2) 5.634 Å
- (3) 5.14 Å
- (4) 2.97 Å
- **48.** Na and Mg crystallize in bcc- and fcc-type crystals, the ratio of number of atoms present in the unit cell of their respective crystal is
 - (1) 1

(2) 0.5

(3)3

- (4)4
- 49. An ionic solid A[⊕]B[⊙] crystallizes as a bcc structure. The distance between cation and anion in the lattice is 338 pm. The edge length of cell is
 - (1) 338 pm
- (2) 390.3 pm
- (3) 292.7 pm
- (4) 507 pm
- **50.** An ionic solid $A^{\oplus}B^{\odot}$ crystallizes as an fcc structure. If the edge length of cell is 508 pm and the radius of anion is 144 pm, the radius of cation is
 - (1) 110 pm
- (2) 364 pm
- (3) 220 pm
- (4) 288 pm
- 51. The γ -form of iron has fcc structure (edge length 386 pm) and β -form has bcc structure (edge length 290 pm). The ratio of density in γ -form and β -form is

- (1) 0.9788
- (2) 1.02

(3) 1.57

- (4) 0.6344
- 52. The density of an ionic compound (Mw = 58.5) is 2.1_{69} kg m⁻³ and the edge length of unit cell is 562 pm, then the closest distance between $A^{\oplus}B^{\ominus}$ and Z_{eff} of unit cell is
 - (1) 281 pm, 4
- (2) 562 pm, 2
- (3) 562 pm, 4
- (4) 281 pm, 2
- 53. The edge length of unit cell of a metal (Mw = 24) having cubic structure is 4.53 Å. If the density of metal is 1.74 g cm^{-3} , the radius of metal is $(N_A = 6 \times 10^{23})$
 - (1) 180 pm
- (2) 160 pm
- (3) 140 pm
- (4) 190 pm
- **54.** The ratio of packing density in fcc, bcc, and cubic structure is, respectively,
 - (1) 1: 0.92: 0.70
- (2) 0.70 : 0.92 : 1
- (3) 1: 0.70: 0.92
- (4) 0.92 : 0.70 : 1
- 55. How many unit cells are present in a cubic-shaped ideal crystal of NaCl of mass 1.0 g?
 - (1) 1.28×10^{21}
- (2) 1.71×10^{21}
- $(3)\ 2.57 \times 10^{21}$
- $(4) 5.14 \times 10^{21}$
- 56. The volume of atoms present in a face-centred cubic unit cell of a metal (*r* is atomic radius) is
 - (1) $\frac{20}{3}\pi r^3$
- $(2) 8\pi r$

(3) $4\pi r^3$

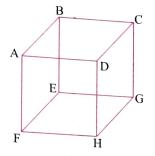
- (4) $\frac{16}{3}\pi r^3$
- 57. An elemental crystal has a density of 8570 kg m⁻³. The packing efficiency is 0.68. If the closest distance between neighbouring atoms is 2.86 Å, the mass of one atom is $(1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg})$
 - (1) 186 amu
- (2) 93 amu
- (3) 46.5 amu
- (4) 43 amu
- 58. The atomic fraction (d) of tin in bronze (fcc) with a density of 7717 kg m⁻³ and a lattice parameter of 3.903 Å is $(Aw \text{ Cu} = 63.54, \text{ Sn} = 118.7, 1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg})$
 - (1) 0.01

(2) 0.05

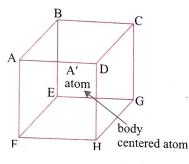
(3) 0.10

- (4) 3.8
- **59.** A metal of density 7.5×10^3 kg m⁻³ has an fcc crystal structure with lattice parameter a = 400 pm. Calculate the number of unit cells present in 0.015 kg of the metal.
 - $(1) 6.250 \times 10^{22}$
- $(2) 3.125 \times 10^{23}$
- (3) 3.125×10^{22}
- $(4) 1.563 \times 10^{22}$
- 60. The ratio of the volume of a tetragonal lattice unit cell that of a hexagonal lattice unit cell is (both having same respective lengths)
 - $(1) \ \frac{\sqrt{3}}{2} abc$
- (2) $\frac{2}{3\sqrt{3}}$
- $(3) \frac{2}{\sqrt{3}} \frac{a^2c}{b}$
- (4) 1

- 61. An fcc lattice has a lattice parameter a = 400 pm. Calculate the molar volume of the lattice including all the empty space.
 - (1) 10.8 mL
- (2) 96 mL
- (3) 8.6 mL
- (4) 9.6 mL
- 62. A metal crystallizes in bcc lattice. The percent fraction of edge length not covered by atom is
 - (1) 10.4%
- (2) 13.4%
- (3) 12.4%
- (4) 11.4%
- 63. In the cubic lattice given below, the three distances between the atoms A–B, A–C, and A–G are, respectively,
 - (1) $a, \sqrt{2}a, \sqrt{3}a$
 - (2) $a, \sqrt{3}a, \sqrt{2}a$
 - (3) $\frac{a}{2}$, $\frac{a}{\sqrt{2}}$, $\frac{\sqrt{3}a}{2}$
 - (4) $a, \frac{\sqrt{3}a}{2}, \sqrt{2}a$



- 64. In body-centred cubic lattice given below, the three distances AB, AC, and AA' are
 - (1) $a, \sqrt{2}a, \frac{\sqrt{3}a}{2}$
 - (2) $a, \frac{\sqrt{3}a}{2}, \sqrt{2}a$
 - (3) $\frac{\sqrt{3}a}{2}$, $\sqrt{2}a$, a
 - (4) $a, \frac{a}{\sqrt{2}}, \frac{\sqrt{3}a}{2}$



- 65. Two ionic solids AB and CB crystallize in the same lattice. If $r_{\rm A^{\oplus}}/r_{\rm B^{\odot}}$ and $r_{\rm C^{\oplus}}/r_{\rm B^{\odot}}$ are 0.50 and 0.70, respectively, then the ratio of edge length of AB and CD is
 - (1) 0.68

(3) 0.88

- (4) 0.98
- **66.** A molecule A_2B (Mw = 166.4) occupies triclinic lattice with a = 5 Å, $\tilde{b} = 8$ Å, and c = 4 Å. If the density of AB₂ is 5.2 g cm⁻³, the number of molecules present in one unit cell is
 - (1) 2

(2) 3

(3)4

- (4)5
- 67. Na and Mg crystallize in bcc- and fcc-type crystals, respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is
 - (1) 4 and 2
- (2) 9 and 14
- (3) 14 and 9
- (4) 2 and 4
- 68. A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atoms at the centre of edges, and Na atom at the centre of the cube. The formula for the compound is

- (1) NaWO₂
- (2) NaWO₃
- (3) Na₂WO₃
- (4) NaWO₄
- 69. The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of 8. The crystal class is
 - (1) Simple cubic
- (2) Body-centred cubic
- (3) Face-centred cubic
- (4) None of these
- 70. The edge length of a face-centred cubic unit cell is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is
 - (1) 144 pm
- (2) 288 pm
- (3) 618 pm
- (4) 398 pm
- 71. In the crystals of which of the following ionic compounds would you expect maximum distance between the centres of the cations and anions?
 - (1) LiF

(2) CsF

(3) CsI

- (4) LiI
- 72. How many kinds of space lattices are possible in a crystal?
 - (1)23

(2)7

- (3)230
- (4) 14
- 73. Potassium crystallizes with a
 - (1) Face-centred cubic lattice
 - (2) Body-centred cubic lattice
 - (3) Simple cubic lattice
 - (4) Orthorhombic lattice
- 74. A compound formed by elements A and B crystallizes in the cubic structure where B atoms are at the face-centres. The formula of the compound is
 - (1)AB₃
- (2)AB
- $(3) A_3 B$
- $(4) A_{2}B_{3}$
- 75. The number of unit cells in 58.5 g of NaCl is nearly
 - $(1) 6 \times 10^{20}$
- $(2) 3 \times 10^{22}$
- $(3) 1.5 \times 10^{23}$
- $(4)\ 0.5 \times 10^{24}$
- **76.** The packing fraction for a body-centred cube is
 - (1) 0.42
- (2) 0.53
- (3) 0.68
- (4) 0.82
- 77. In NaCl, the chloride ions occupy the space in a fashion of
 - (1) fcc

- (2) bcc
- (3) Both
- (4) None
- 78. The range of radius ratio (cationic to anionic) for an octahedral arrangement of ions in an ionic solid is
 - (1) 0.155 0.225
- (2) 0.225-0.414
- (3) 0.414 0.732
- (4) 0.732 1.000
- 79. When molten zinc is cooled to solid state, it assumes hep structure. Then the number of nearest neighbours of zinc atom will be
 - (1)4

(2)6

(3) 8

- (4) 12
- 80. The interionic distance for cesium chloride crystal will be
 - (1) a

- (3) $\sqrt{3}a/2$
- (4) $2a/\sqrt{3}$

of. In the structure of the	1 1 1 1 1 1	(3) 1	(4) 8
(1) 0, 0, 0, and $\frac{1}{2}$, $\frac{1}{2}$	$\frac{1}{2}$ (2) $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$, and $\frac{1}{2}$, $\frac{1}{2}$	91. What is the coordinate	ation number of Th ⁴⁺ in ThO ₂ ?
		(1) 4	(2) 8
(3) 0, 0, 0, and $\frac{1}{4}$, $\frac{1}{4}$	$\frac{1}{4}$ (4) 0, 0, 0, and $\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$	(3) 6	(4) 12
82. Which of following	statements is correct in the zinc-	92. The coordination respectively,	number Cs and Br in CsBr are
blende-type structure	of an ionic compound?	(1) 8, 8	(2) 6, 6
	mber of each cation and anion is 2.	(3) 8, 6	(4) 6, 8
(3) Coordination nur	mber of each cation and union is 4. The state of each cation and union is 6. The state of each cation and union is 8.	93. Fraction of total vocube is	lume occupied by atoms in a simple
	oic unit cell of closest packed atoms,	(1) $\sqrt{3}\pi/8$	(2) $\pi/6$
•	a terms of edge length a of the unit	$(3) \pi/3$	$(4) \sqrt{2}\pi/3$
(1) $a/2$	(2) $a/\sqrt{2}$	94. Xenon crystallizes i	n fcc lattice and the edge of the uni
(3) $a/2\sqrt{2}$	(4) $\sqrt{3}a/4$	_	the radius of Xe atom is
· /	ing expressions is correct in the case	(1) 219.20 pm	(2) 438.5 pm
of a sodium chloride	unit cell (edge length, a)?	(3) 290.3 pm	(4) 318.53 pm
$(1) r_{\oplus} + r_{\odot} = a$			e structure), Mg ²⁺ is introduced in
$(3) r_{\oplus} + r_{\odot} = 2a$	$(4) r_{\oplus} + r_{\odot} = \sqrt{2a}$		coordination numbers of Be ²⁺ and
4 out of 8 TVs are al	atoms form fcc arrangement where so occupied by Si atoms. $Z_{\rm eff}$ of unit	Mg^{2+} are, respective (1) 8, 8	(2) 6, 6
cell is	(2) 2	(3) 4, 4	(4) 8, 6
(1) 1 (3) 4 86. Which of the follow	(2) 2 (4) 8 ing crystal systems exist in bc, end-		ved from a single body diagonal in ping, then the molecular formula of
centred, fc, as well a		the unit cell would b	
(1) Hexagonal	(2) Cubic	(1) $Mg_2Be_{3.5}O_{2.5}$	(2) $Mg_3Be_3O_{3.75}$
(3) Triclinic	(4) Orthorhombic	(3) $Mg_3Be_3O_{3.5}$	(4) $Mg_4Be_4O_{3.5}$
	A atoms are present on alternative		, , 5.5
atoms are present or	e present on alternate faces, and C a alternate edges and body centre of est formula of the compound is	97. In spinel, Mg ²⁺ is pr lattice of oxide ions the OVs. The formul	esent in one-eighth of TVs in an fee and Al ³⁺ ions are present in half of a of spinel is
$(1) A_2 BC_4$	$(2) AB_2C_4$	$(1) \text{MgAl}_3 \text{O}_3$	(2) MgAl ₂ O ₃
(3) ABC ₄	(4) ABC ₂	$(3) \text{ MgAl}_2\text{O}_4$	(4) MgAl ₃ O ₄
88. Which of the following	ng statements is correct for the body-	2 4	J ,
centred cubic structu	re of an ionic compound?	Tetrahedral and Octahed	
(1) Coordination num	mber of each cation and anion is 2.	98. How many nearest n	eighbours are there in an atom or io
(2) Coordination num	mber of each cation and anion is 4.		e of a closed packed structure?
(3) Coordination num	mber of each cation and anion is 6.	(1) 4	(2) 6
(4) Coordination num	mber of each cation and anion is 8.	(3) 8	(4) 12
	has a density of 2.72 g cm ⁻³ and	respectively does no	t" and "next nearest" neighbours
crystallizes in a cul	oic lattice with an edge of 404 pm.	(1) 8, 8	tassium have in bcc lattice?
Which of the follow		(3) 6, 8	(2) 8, 6
(1) It forms bcc unit		100. The unit cell of diame	(4) 6, 6
(2) It forms fcc unit (3) Its CN = 8	cell	(1) 6 carbon atoms 4	atoms constitute ccp and two atomb
(4) Its CN is 6		occupy half of oc	tahedral voids
90. ThO ₂ exists in fluo	rite structure, what is the effective on in the unit cell of ThO ₂ ?	(2) 8 carbon atom, 4 occupy all the oct	4 atoms constitute cop and 4 atoms
	· · · · · · · · · · · · · · · · · · ·	(3) 8 carbon atoms, 4	4 atoms form fcc lattice and 4 atoms e tetrahedral voids alternately

(2) 4

(4) 8

(1) 2

(3) 1

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81. In the structure of diamond, carbon atoms appear at

- (4) 12 carbon atoms, 4 atoms form fcc lattice and 8 atoms occupy all the tetrahedral holes
- 101. In diamond, the coordination number of carbon is:
 - (1) Four and its unit cell has eight of carbon atoms
 - (2) Four and its unit cell has six carbon atoms
 - (3) Six and its unit cell has four carbon atoms
 - (4) Four and its unit cell has four carbon atoms
- 102 In diamond, carbon atom occupy fee lattice points as well as alternate tetrahedral voids. If edge length of the unit cell is 356 pm, then diameter of carbon atom is:
 - (1) 77.07 pm
- (2) 154.14 pm
- (3) 251.7 pm
- (4) 89 pm
- 103. The distance between an octahedral and tetrahedral void in fcc lattice would be:
 - $(1) \sqrt{3}a$

- $(2) \ \frac{\sqrt{3}a}{2}$
- $(3) \ \frac{\sqrt{3}a}{3}$
- (4) $\frac{\sqrt{3}a}{4}$
- **104.** In the rock salt *AB*, of *C* introduced in tetrahedral voids such that no distortion occurs, then formula of resultant compound is:
 - (1) ABC
- $(2) ABC_{2}$
- $(3) A_4 B_4 C$
- $(4) ABC_{8}$
- 105. How many tetrahedral holes are occupied in diamond?
 - (1) 25%
- (2) 50%
- (3)75%
- (4) 100%
- **106.** Total number of voids in 0.5 mole of a compound forming hexagonal closed packed structure are
 - $(1) 6.022 \times 10^{23}$
- (2) 3.011×10^{23}
- $(3) 9.034 \times 10^{23}$
- $(4) 4.516 \times 10^{23}$
- 107. The melting point of RbBr is 682°C, while that of NaF is 988°C. The principal reason that melting point of NaF is much higher than that of RbBr is that:
 - (1) The two crystals are not isomorphous
 - (2) The molar mass of NaF is smaller than thet of RbBr
 - (3) The internuclear distance $r_c + r_a$ is greater for RbBr than for NaF
 - (4) The bond in RbBr has more covalent character than the bond in NaF
- 108. Which of the crystals have same general formula?
 - (1) Rock salt type and Anti-fluorite type
 - (2) Rock salt type and Fluorite type
 - (3) Fluorite type and CsCl type
 - (4) Sphalerite type and Rock salt type A_4B_4 or AB.
- 109. A non stiochiometric compound Cu_{1.8}S is formed due to incorporation of Cu²⁺ ions in the lattice of cuprous sulphide. What percentage of Cu²⁺ ion in the total copper content is present in the compound?
 - (1)88.88
- (2) 11.11
- (3)99.8
- (4)89.8

- 110. In the closest packing of atoms
 - (1) The size of TV is greater than that of OV.
 - (2) The size of TV is smaller than that of OV.
 - (3) The size of TV is equal to that of OV.
 - (4) The size of TV may be greater or smaller or equal to that of OV depending upon the size of atoms.
- 111. In a closed packed structure of mixed oxides, the lattice is composed of mixed oxides ions. One-eighth of tetrahedral voids are occupied by divalent cations (A²⁺) while one-half of octahedral voids are occupied by trivalent cations (B³⁺). The formula of mixed oxide is
 - $(1) A_2 BO_3$
- (2) AB₂O₃
- $(3) A_2 BO_4$
- $(4) AB_2O_4$
- 112. If R is the radius of the octahedral voids and r is the radius of the atom in close packing, then r/R is equal to
 - (1) 2.41
- (2)4.76
- (3) 3.22
- (4)9.1
- 113. Every atom or ion that forms an fcc unit cell is surrounded by
 - (1) Six OVs and eight TVs.
 - (2) Eight OVs and six TVs.
 - (3) Six OVs and six TVs.
 - (4) Eight OVs and four TVs.
- 114. Consider the structure of CsCl (8: 8 coordination). How many Cs[⊕] ions occupy the second nearest neighbour locations of a Cs[⊕] ion?
 - (1) 8

(2)24

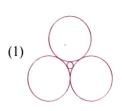
(3)6

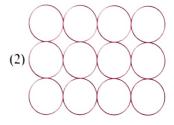
- (4) 16
- 115. A TV in fcc is formed by atoms at
 - (1) 3 corners + 1 face centre
 - (2) 3 face centres + 1 corner
 - (3) 2 face centres + 2 corners
 - (4) 2 face centres + 1 corner + 1 body centre
- 116. The number of octahedral sites per sphere in fcc structure is
 - (1) 8

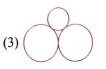
(2) 4

(3)2

- (4) 1
- 117. Which of the following figures represents the cross section of an OV?









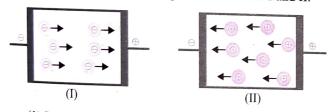
	Physical Chemistry						(2) 000	00	
118.	The fraction of octahedral vo	ids filled by Al ³⁺ ions in Al ₂ O ₃		$(1) 0^{\circ}, 90^{\circ}$			(2) 90°,		
	$(r_{Al^{3}\oplus}/r_{O^{2-}}=0.43)$ is			(3) 30°, 90		يحا امي	(4) 90°,	30°	
	(1) 0.43	(2) 0.287	128.	Levitation	is achiev	vea by	n	ant mass	
	(3) 0.667	(4) 1		(1) Mutua	repuisio ctor	n betwee	en perman	ent magr	iet and a supp
119.	In the closest packing of ato			(2) Mutua		sion bet	tween a	weak m	agnet .
1177		two octahedral voids per atom		superc	onductor	•			and and
	(2) Two tetrahedral voids an	d one octahedral void per atom		(3) A sligh			een a per	manent	magnet and
, ,	(3) Two of each tetrahedral	and octahedral voids per atom			onductor				
	(4) One of each tetrahedral a	and octahedral void per atom		(4) None (
120.		half of the edge-centred OVs	129.	Which one		pervoski			
1200	in RbBr, then the molecular	formula of unit cell is		(1) BaTiO	-		(2) NaM		
		(2) $Rb_{1.5}Br_3$		(3) BaTiO	2	2	(4) NaM		11.
	2 2	(4) Rb ₄ Br _{2.5}	130.	Due to Fre		ect, the			c solids
Dofo	cts in Crystals	2.0		(1) Increas			(2) Decr		
	-	y form interstitial compounds,		(3) Does n	_		(4) Char	-	
121.	the non-metal;s (H, B, C, N		131.	Which of		wing is i			compound
	(1) Voids or holes in cubic-p			(1) Rochel			(2) $K_4[F]$	•	
	(2) Tetrahedral voids			(3) BaTiO			(4) KH ₂	,	
	(3) Octahedral voids		132.	The mater	ial used	ın solar		ains	
	(4) All of these			(1) Cs			(2) Si		
122.	-	n is bonded to four other carbon		(3) Sn	_		(4) Ti		
	•	e tetrahedral voids are occupied	133.	What type	of crysta	defect	is indicate	ed in the o	11agram give
	is:	er of carbon atoms per unit cell		below	0	A	G19	A	.
	(1) 4	(2) 6		Na [⊕] Cl [⊝]	Cl [⊖]	Na [⊕]	Cl [⊖]	Na [⊕]	Cl [⊖] Cl [⊖]
	(3) 8	(4) 12		Na [⊕]	L Cl [©]	Cl [⊙]	Na [⊕] Cl [⊕]	∟∟ Na [⊕]	Cl [⊖]
123.	If an element (at. mass = 50) crystallises in fcc lattice, with		Cl [⊖]	Na [⊕]	Cl [©]	Na [⊕]		Na [⊕]
		ensity of unit cell if it contains		(1) Both F	renkel ar	nd Schot	tky defec	ts.	
	0.25% Schottky defects (use	11		(2) Schottl			inty derec		
	(1) 2.0 g/cc	(2) 2.66 g /cc(4) None of these		(3) Intersti	tial defe	ct			
124	(3) 3.06 g/cc	aphic (AgBr) paper, silver atoms		(4) Frenke	l defect				
124.	move in through these defe		134.	Silicon de	opped w	ith gro	up 13 an	d group	15 membe
	(1) Form –ve images			elements i	s, respec	tively, c	alled	semicor	nductor
	(2) Form tiny clumps of silv	ver atoms		(1) p -type,	n-type		(2) n -typ		e
	(3) Form a colour image		125	(3) <i>p</i> -type			(4) n-typ		
	(4) None of the above		135.	The electr $(1) 10^8$ oh:	ical cond	luctivity	of semic	onductor	is
125.		mpurity in a crystal lattice of		$(1) 10^{-0.00}$ $(2) 10^{-2.2}$ c		-1			
	C	semicondctor formation will		(3) In the			$10^2 \mathrm{ohm}^{-1}$	cm^{-1}	
	occur?	(2) <i>n</i> -type		(4) None (_		ro omn	CITT	
	(1) <i>p</i> -type (3) Both (1) and (2)	(4) None of these	136.	Pure silico	on and ge	ermaniui	m are		
126	Which of the following stat			(1) Condu	ctors				
120.	(1) Piezo-electricity is due			(2) Insulat					
		to alignment of dipoles in same		(3) Semice					
	direction		137	(4) May be					10
	(3) Pyro-electricity is due t	o heating polar crystals	13/,	Which of		wing is a			
	(4) All of the above			(1) BaTiO	3		(2) $K_4[F]$	$e(CN)_6$	
127		rder diffraction, spacing between		$(3) Pb_2O_3$			(4) None	e of these	e
	two planes respectively are	λ and $\frac{\lambda}{2}$							
		-							

- 138. Schottky defect to crystals is observed when
 - (1) Unequal number of cations and anions are missing from the lattice.
 - (2) Equal number of cations and anions are missing from the lattice.
 - (3) An ion leaves its normal site and occupies an interstitial site.
 - (4) Density of the crystal is increased.
- 139. Which of the following has Frenkel defect?
 - (1) Sodium chloride
- (2) Graphite
- (3) Silver bromide
- (4) Diamond
- **140.** To get *n*-type doped semiconductor, impurity to be added to silicon should have the following number of valence electrons
 - (1) 2

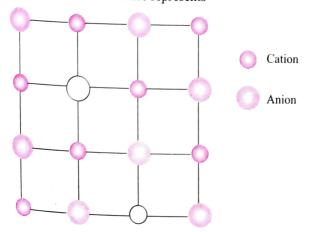
(2)5

(3) 3

- (4) 1
- 141. Superconductors are derived from the compounds of
 - (1) p-block elements
- (2) Lanthanides
- (3) Actinides
- (4) Transition elements
- 142. A semiconductor of Ge can be made p-type by adding
 - (1) Trivalent impurity
- (2) Tetravalent impurity
- (3) Pentavalent impurity
- (4) Divalent impurity
- 143. Which of the following metal oxides is anti-ferromagnetic in nature?
 - $(1) \text{ MnO}_{2}$
- (2) TiO₂
- (3) VO₂
- (4) CrO₂
- 144. What are types of following semiconductors I and II.

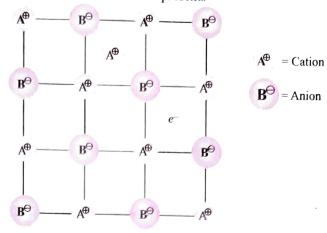


- (1) I \Rightarrow *p*-type, II \Rightarrow *n*-type (2) I \Rightarrow *n*-type, II \Rightarrow *p*-type
- (3) Both *n*-type
- (4) Both *p*-type
- 145. The structure shown here represents



- (1) Schottky defect
- (2) Frenkel defect
- (3) Metal excess defect
- (4) None

146. The structure shown here represents



- (1) Schottky defect
- (2) Frenkel defect
- (3) Metal excess defect because of absent anion
- (4) Metal excess defect because of excess cation
- 147. In AgCl, the Ag[⊕] ions are displaced from their lattice position to an interstitial position. Such a defect is called
 - (1) Schottky defect
- (2) Frenkel defect
- (3) Wadsley defect
- (4) Colour centre
- **148.** NaCl shows Schottky defects and AgCl shows Frenkel defects. Their electrical conductivity is due to the
 - (1) Motion of electrons and not the motion of ions
 - (2) Motion of ions and not the motion of electrons
 - (3) Lower coordination number of NaCl
 - (4) Higher coordination number of AgCl
- 149. Amorphous solids are classified as
 - (1) Isotropic and supercooled liquids
 - (2) Anisotropic and supercooled liquids
 - (3) Isoenthalpic and supercooled liquids
 - (4) Isotropic and superheated solids
- 150. Due of Frenkel defect
 - (1) Density of the crystal decreases
 - (2) Conduction increases
 - (3) Conduction decreases
 - (4) Crystal becomes charged electrically
- 151. Which of the following statements is/are correct?
 - (1) All ferroelectric solids are piezoelectric.
 - (2) All piezoelectric solids are ferroelectric.
 - (3) Lead zirconate (PbZrO₃) is an antiferroelectric crystal.
 - (4) BaTiO₃ (barium titanate) is a ferroelectric crystal.
- 152. Which of the following statements is/are correct?
 - (1) A diode is a combination of *p* and *n*-type semiconductors which is used as a rectifier.
 - (2) Transistors are sandwich semiconductors of the type *pnp* or *npn* which are used to detect or amplify radio or audio signals.
 - (3) Monoxides of transition metals, all of which possess NaCl structures, show very large variations in electrical properties.
 - (4) ReO₃ has the conductivity as well as appearance like that of copper.

- 153. Which of the following statements is/are correct?
 - (1) Piezoelectric crystals are used as pick-ups in record players, they are also used in microphones, ultrasonic generators, and sonar detectors.
 - (2) BaTiO₃, Rochelle salt, KH₂PO₄, and quartz are ferroelectric and piezoelectric solids.
 - (3) The temperature above which no ferromagnetism is observed is called curie temperature.
 - (4) The temperature at which the material shows superconductivity is called transition termperature.

Miscellaneous

154. Nearest distance between two tetrahedral voids and between two octahedral voids are respectively.

$$(1) \ \frac{a}{\sqrt{2}}, \frac{\sqrt{3}}{a} a$$

(2)
$$\frac{\sqrt{3}}{4}a, \frac{\sqrt{3}}{2}a$$

$$(3) \ \frac{\sqrt{3}}{2} a, \frac{a}{\sqrt{2}}$$

(4)
$$\frac{\sqrt{3}}{2}a, \frac{\sqrt{3}}{4}a$$

- **155.** In sphalerite and antifluorite type structures, number of tetrahedral voids occupied are respectively.
 - (1) 8, 4

(2)4,8

(3)4,0

- (4) 0, 4
- **156.** Choose the correct option for hexagonal close packing of sphere in three dimensions
 - (1) In one unit cell there are 12 octahedral voids and all are completely inside the unit cell.
 - (2) In one unit cell there are six octahedral voids and all are completely inside the unit cell.
 - (3) In one unit cell there are six octahedral voids and of which three are completely inside the unit cell and other three are from contributions of octahedral voids which are partially inside the unit cell.
 - (4) In one unit cell there are 12 tetrahedral voids, all are completely inside the unit cell.
- 157. In a hexagonal closed packed system of crystals. assume, $C = 2 \times \text{distance}$ between two close packed layers, and (r) is the radius of every sphere.

The number of effective atoms and $\left(\frac{C}{r}\right)$ ratio in this hop unit cell are respectively.

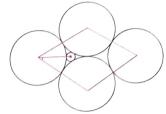
- (1) 8, $24\sqrt{2} r^3$
- (2) 6, $4 \times \sqrt{\frac{2}{3}}$
- (3) 12, $24\sqrt{2} r^3$
- (4) 12, $4 \times \sqrt{\frac{2}{3}}$
- **158.** In rutile structure coordination number of cation and anion are respectively.
 - (1) 6, 3

(2) 3, 6

(3) 6, 4

- (4)4,6
- **159.** In spinel structure, ratio of tetrahedral to octahedral voids occupied and unoccupied are respectively:
 - (1) 1:2 and 2:1
- (2) 7:2 and 1:2
- (3) 2:1 and 2:1
- (4) 2:7 and 2:1

- 160. If the radii of Mg²⁺, Cs[⊕], O²⁻, S²⁻ and Cl[⊕] ions are 0_{fot} 1.69, 1.40, 1.84, and 1.81 Å, respectively. The coordination number of the cations in the crystals of CsCl, MgS and Mg are respectively
 - (1) 4, 8 and 6
- (2) 6, 4 and 8
- (3) 8, 4 and 6
- (4) 6, 6 and 8
- 161. Consider the parallelogram shown in the figure below representing two-dimensional unit cell. If R is the radius larger circle and r is the radius of the triangular hole, we relation between r and R is:



$$(1) r = \left(\frac{2}{\sqrt{3}}\right) R$$

$$(2) r = \left(\frac{\sqrt{2}}{3}\right) R$$

$$(3) r = \left(\frac{2}{\sqrt{3}} - 1\right) R$$

$$(4) r = \left(\frac{\sqrt{2}}{3} - 1\right) R$$

- 162. There are five types of 2D- lattice which differ in the symmetry of arrangement of points. Which of the following 2D-lattice is not possible
 - (1) Hexagonal
- (2) Pentagonal
- (3) Parallelogram
- (4) Rectangular
- 163. Metallic gold crystallises in the fcc lattice. The length of the cubic unit cell is a = 4,242 Å.

Closest distance between two gold atoms and packing factor are respectively.

(1) 3.0 A°,
$$\frac{\sqrt{2}}{6}$$
 π

(2) 1.5 A°
$$\frac{\sqrt{2}}{6}\pi$$

(3) 3.0
$$A^{o}$$
, $\frac{\sqrt{3}}{8}\pi$

(4)
$$1.5 \,\mathrm{A_o^o}, \, \frac{\sqrt{3}}{8} \,\pi$$

- **164.** Which of the following statements is INCORRECT for by diamond structure?
 - (1) Each atom has 4 nearest neighbours and 12 next nearest neighbours.
 - (2) It is relatively empty.
 - (3) The maximum proportion of the available volume which may be filed by hard spheres is only 0.34.
 - (4) The maximum proportion of the available volume which may be filled by hard spheres is only 0.46.
- 165. Which of the following statements is/are correct?
 - I. Piezoelectric crystals are used as pick-ups in record players, they are also used in microphones, ultrasopti generators, and sonar detectors.
 - II. BaTiO₃, Rochelle salt, KH₂PO₄, and quartz aff ferroelectric and piezoelectric solids.
 - III. The temperature above which no ferromagnetismic observed is called transition temperature.

- IV. The temperature at which the material shows superconductivity is called curie temperature.
- (1) I, II

- (2) II, III, IV
- (3) I, II, III
- (4) All

Multiple Correct Answers Type



Classification of Solids and Their Properties

- 1. An hcp and a ccp structure for a given element would be expected to have
 - (1) The same coordination number
 - (2) The same density
 - (3) The same packing fraction
 - (4) All of these
- 2. Ions of NaCl which are touched by 1 body diagonal are
 - (1) Cl[⊙] ions present at the corner of cube
 - (2) Cl[©] ions present at the face centre of cube
 - (3) Na[⊕] ions present at the edge centre of cube
 - (4) Na[®] present at body centre of cube
- 3. Which of the following statements is/are correct for both fluorite and antifluorite structures?
 - (1) Cation is present in alternate TVs.
 - (2) Anion constitutes lattice.
 - (3) Number of formula unit in one unit cell is 4.
 - (4) 100% tetrahedral voids are occupied.
- 4. Identical spheres are undergoing two-dimensional packing in square close packing and hexagonal close packing. Which is correct regarding the spheres?
 - (1) The ratio of coordination number for a sphere in first case to that in second case is 2:3.
 - (2)Packing in second case is more effective.
 - (3)Packing in first case is more effective.
 - (4)The stacking of layer on first type packing produces simple cubic structure.
- 5. For which of the following cases, answer is 4?
 - (1) Coordination number of Zn^{2+} in Zinc blende
 - (2) Number of body diagonal planes in a cube
 - (3) Formula units in rock salt structure
 - (4) Formula units in CsCl structure
- 6. An octahedron has
 - (1) 8 corners
- (2) 8 faces
- (3) 8 edges
- (4) 12 edges
- 7. Aluminium metal has a density of 2.72 g cm⁻³ and crystallizes in a cubic lattice with an edge of 404 pm. Which is/are correct?
 - (1) It forms an fcc unit cell.
 - (2) It forms a bcc unit cell.
 - (3) Its coordination number is 8.
 - (4) Its coordination number is 12.

- **8.** If the radius of anion is 0.20 nm, the maximum radius of cations which can be filled in respective voids is correctly matched in
 - (1) $r_{\oplus} = 0.0828$ nm for tetrahedral void
 - (2) r_{\oplus} = 0.045 nm for triangular void
 - (3) r_{\oplus} = 0.1464 nm for octahedral void
 - (4) None of the above
- 9. Select the correct statement(s) about three-dimensional hcp system.
 - (1) The umber of atoms in hcp unit cell is six.
 - (2) The volume of hcp unit cell is $24\sqrt{2} r^3$.
 - (3) The empty space in hcp unit cell is 26%.
 - (4) The base area of hcp unit cell is $6\sqrt{3} r^2$.
- 10. In which of the following systems primitives $a \neq b \neq c$?
 - (1) Orthorhombic
- (2) Monoclinic
- (3) Triclinic
- (4) Hexagonal
- 11. In which of the following systems interfacial angles $\alpha = \gamma = 90^{\circ}$ but $\beta \neq 90^{\circ}$?
 - (1) Monoclinic
- (2) Rhombohedral
- (3) Triclinic
- (4) Hexagonal
- 12. The space in which atoms are not present in unit cell is
 - (1) In sc 48%
- (2) In fcc 26%
- (3) In bcc 32%
- (4) In hexagonal 26%
- 13. Which of the following having their radius ratio between 0.414 and 0.732, i.e., for NaCl structure, have their radius ratio not in this range but possess NaCl-type structure?
 - (1) LiBr

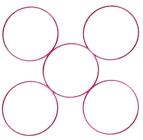
- (2) KC1
- (3) RbCl
- (4) BaO
- 14. In the fluorite structure if the radius ratio is $\left(\sqrt{\frac{3}{2}} 1\right)$. how many ions does each cation touch?
 - (1) 4 anions
- (2) 12 cations
- (3) 8 anions
- (4) No cations
- **15.** If the radius of $Cs^{\oplus} = 1.69 \text{ Å}$ and $Br^{\ominus} = 1.95 \text{ Å}$, then which of the following is/are correct statement?
 - (1) The edge length of unit cell is 4.2 Å.
 - (2) The coordination number for Cs^{\oplus} is 6.
 - (3) CsBr has bcc-type structure.
 - (4) Br^{\odot} ions touch each other along the edge.
- **16.** Given is the arrangement of atoms in a crystallographic plane.
 - Which plane correctly represent(s) the adjacent drawn structure?
 - (1) Face plane in fcc
 - (2) Body diagonal plane in fee
 - (3) Face plane in bcc
 - (4) Body diagonal plane in bcc



- 17. Graphite is
 - (1) A good conductor
- (2) sp² hybridized
- (3) An amorphous solid
- (4) A covalent crystal
- 18. Diamond is
 - (1) A covalent solid
- (2) A non-conductor
- (3) A lubricant
- (4) sp³ hybridized
- 19. The density of KBr is 2.75 g cm⁻³. The length of the unit cell is 654 pm. Atomic mass of K = 39, Br = 80. Then what is true about the predicted nature of the solid?
 - (1) The unit cell is fcc.
 - (2) Z = 4.
 - (3) There are four constituents/unit cells.
 - (4) There are 8 ions at corners and 6 at the centres of the faces.
- 20. What is true about a bcc unit cell?
 - (1) The number of atoms in the unit cell is 2.
 - (2) In addition to an atom at the centre of the body, in a unit cell there are 8 atoms at 8 different corners.
 - (3) One-eighth of an atom at a corner of the unit cell.
 - (4) None of the above.
- 21. What is true about simple cubic type of unit cells?
 - (1) Eight constituents are at different corners of the cube.

 - (3) Contribution by one corner is 1/8th of an atom.
 - (4) None of the above.
- 22. Which of the following is/are covalent solids?
 - (1) Fe
- (2) Diamond (3) NaCl
- (4) Graphite
- 23. Which is/are not amorphous solid(s)?
 - (1) Rubber
- (2) Graphite (3) Glass
- (4) Plastics
- 24. Which is/are correct statement?
 - (1) Packing fraction in 2D-hcp is 0.785
 - (2) Packing fraction in AAA.... is 0.52
 - (3) Packing fraction in ABAB..... is 0.74
 - (4) Void fraction in ABCABC...... is 0.26
- **25.** Given: Radius of $A^{2+} = 100$ pm; Radius of $C^{\oplus} = 240$ pm; Radius of $B^{2-} = 300$ pm; Radius of $D^{\Theta} = 480$ pm Which is/ are correct statement?
 - (1) Coordination number of A^{2+} in compound AB is 4
 - (2) Coordination number of A^{2+} in compound AB is 6
 - (3) Coordination number of C^{\oplus} in compound CD is 6
 - (4) Coordination number of C^{\oplus} in compound CD is 8
- 26. If the three interaxial angles defining the unit cell are all equal in magnitude, the crystal cannot belong to the
 - (1) Orthorhombic system (2) Cubic system
- - (3) Hexagonal system
- (4) Triclinic system
- 27. Crystal systems in which no two axial lengths are equal
 - (1) Tetragonal
- (2) Orthorhombic
- (3) Monoclinic
- (4) Triclinic

- 28. Given is the arrangement of atoms in crystallograph, plane. Which plane correctly represent(s) the draw structure?
 - (1) Face plane in fcc
- (2) Body diagonal plane in fo
- (3) Face plane in bcc
- (4) Body diagonal plane in he



- 29. Potassium crystallizes in body-centred cubic lattice. Then
 - (1) The distance between nearest neighbors is 4.50 Å
 - (2) The distance between next-nearest neighbors is 5.201
 - (3) Each K have nearest neighbors equal to 4.
 - (4) Each K have nearest neighbors equal to 6.

Tetrahedral and Octahedral Voids

- 30. Position of OVs in an fcc structure is
 - (1) Corners of unit cell
 - (2) Edge centre of unit cell
 - (3) Body centre of unit cell
 - (4) Face centre of unit cell
- 31. For the spinel structure (MgAl₂O₄), the correct statement
 - (1) 50% OVs are occupied by ions.
 - (2) Al³⁺ is equally distributed in TVs and OVs.
 - (3) Oxide ions occupy ccp lattice.
 - (4) 12.5% TVs are occupied by ions.
- 32. Following three planes (P₁, P₂, P₃) in an fcc unit cell at shown in the figure below. Consider the following statements and choose the correct option/options that follow:







- (1) P₁ contains no three-dimensional voids.
- (2) P₂ contains only octahedral voids.
- (3) P₃ contains both octahedral and tetrahedral voids.
- (4) All of these
- 33. Position of octahedral voids in fcc structure is/are
 - (1) Edge centre of unit cell
 - (2) Body centre of unit cell
 - (3) Corners of unit cell
 - (4) Face centre of unit cell

- 34. Position of TVs in closest packed structure is/are
 - (1) Edge centre of unit cell
 - (2) Two TVs on each body diagonal
 - (3) Position of each TV from corner is $\sqrt{3}a/4$.
 - (4) Face centre of unit cell
- 35. Which of the following statements is/are correct about TVs in an fcc unit cell?
 - (1) Number of TVs per atom in fcc unit cell is 2.
 - (2) Number of TVs per unit cell is 8.
 - (3) Number of TVs is twice the number of atoms in the fcc unit cell.
 - (4) Number of TVs is equal to the number of atoms in the fcc unit cell.
- **36.** Which of the following statements is/are correct about TVs in an fcc unit cell?

Given: Edge length = a

Body diagonal = b

- (1) Each TV lies at a distance b/4 from the nearest corner.
- (2) Each TV lies at a distance 3b/4 from the farthest corner.
- (3) Each TV lies at a distance of $\sqrt{3}a/4$ from the nearest corner.
- (4) The distance between two TVs is b/2.
- 37. If the radius of Na^{\oplus} is 95 pm and that of Cl^{Θ} ions is 181 pm then:
 - (1) Co-ordination no. of Na^{\oplus} is 6
 - (2) Co-ordination no. of Cl[⊖] is 8
 - (3) Length of the unit cell is 552 pm
 - (4) Length of the unit cell is 380 pm
- **38.** Select the correct statement(s):
 - (1) A NaCl type AB crystal lattice can be interpreted to be of two indiviadual fcc type unit lattice of A^{\oplus} and B^{\ominus} fused together in such amanner that the corner of one unit lattice becomes the edge centre of the other
 - (2) In a fcc unit cell, the body centre is an octahedral void
 - (3) In an sc lattice, there can be no octahedral void
 - (4) In an sc lattice, the body centre is the octahedral void
- 39. Which of the following is not true about the voids formed in 3 dimensional hexagonal close packed structure?
 - (1) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer
 - (2) All the triangular voids are not covered by the spheres of the second layer
 - (3) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap

- (4) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer
- **40.** The co-ordination number of fcc structure for metals is 12, since
 - (1) Each atom touches 4 others in same layer, 3 in layer above and 3 in layer below
 - (2) Each atom touches 4 others in same layer, 4 in layer above and 4 in layer below
 - (3) Each atom touches 6 others in same layer, 3 in layer above and 3 in layer below
 - (4) Each atom touches 3 others in same layer, 6 in layer above and 6 in layer below
- **41.** In the unit cell of NaCl, which of the following statement are correct?
 - (1) Na^{\oplus} ions have six Cl^{Θ} ions in its nearest neighbourhood
 - (2) Cl^{Θ} ion have six Na^{\oplus} ion in its nearest neighbourhood
 - (3) Second nearest neighbour of Na[⊕] ion are twelve Na[⊕] ions
 - (4) NaCl has 68% of occupied space.
- **42.** Sodium oxide Na₂O is a crystalline solid. It has:
 - (1) Antifluorite structure
 - (2) Na^{\oplus} ions are present at body diagonals
 - (3) Na^{\oplus} ions are present at tetrahedral voids
 - (4) O²⁻ ions are present at octahedral voids
- 43. Select the correct statements among the following:
 - (1) Nearest neighbour distance in NaCl = $\frac{a}{2}$
 - (2) Nearest neighbour distance in $CaF_2 = \frac{a\sqrt{3}}{4}$
 - (3) Nearest neighour distance in Na₂O = $\frac{a\sqrt{3}}{4}$
 - (4) Nearest neighour distace in CsCl = $\frac{a\sqrt{3}}{2}$

Defects in crystals

- 44. Which of the following statements is/are correct?
 - (1) Dislocation of ion from lattice site to interstitial site is called Frenkel defect.
 - (2) Missing of +ve and -ve ions from their respective position producing a pair of holes is called Schottky defect.
 - (3) The presence of ions in the vacant interstital sites along with lattice point is called interstital defect.
 - (4) Non-stoichiometric NaCl is yellow solid.
- **45.** Select the correct statement(s).
 - (1) The conductance through electrons is called *p*-type conduction.

- (2) The conductance through positive holes is called *p*-type conduction.
- (3) The conductance through electrons is called *n*-type conduction.
- (4) The band gap in germanium is small.
- **46.** Select the correct statement(s).
 - (1) Solids with F-centres are paramagnetic.
 - (2) Ferrimagnetic character of Fe₃O₄ at room temperature changes to paramagnetic character at 850 K.
 - (3) Anti-ferrimagnetic V_2O_3 changes to paramagnetic at 150 K.
 - (4) Non-stoichiometric Cu₂O is a *p*-type semiconductor.
- 47. Non-stoichiometric compounds are
 - (1) Cu₂O

(2) Cu₂S

(3) FeO

- (4) Hg₂Ba₂YCaCu₂O₇
- 48. Recently discovered superconductivity materials are
 - $(1) M_3 C_{60}$

(2) YBa₂Cu₃O₇

(3) SiC

- (4) Hg₂Ba₂YCaCu₂O₇
- 49. If a mixture of LiCl and NaCl is melted and then cooled,
 - (1) A solid solution is formed.
 - (2) Mixture formed is called eutectic mixture.
 - (3) TiO_{1.8} is non-stoichiometric solid solution of Ti₂O₃ and TiO₂.
 - (4) Neither LiCl nor NaCl separates.
- **50.** Which of the following statements is/are correct?
 - (1) If three Fe²⁺ ions are missing from their lattice in FeO, then there must be two Fe³⁺ ions somewhere in the lattice.
 - (2) Crystals with metal deficiency defects are called super conductors.
 - (3) Crystals with metal deficiency are called semiconductors.
 - (4) 1 Bohr Magneton = $9.27 \times 10^{-24} \,\mathrm{Am}^2$
- **51.** Select the correct statement(s).
 - (1) The non-stoichiometric form of NaCl is yellow and that of KCl is blue-lilac.
 - (2) Solids containing F-centres (Farbe) are paramagentic.
 - (3) Non-stoichiometric compounds are called Berthollide compounds.
 - (4) Conduction by electrons is called *n*-type semiconductors.
- **52.** A mineral having the formula AB₂ crystallizes in the ccp lattice, with A atoms occupying the lattice points. Select the correct statement(s).
 - (1) The coordination number (CN) for A atoms = 8.
 - (2) The CN for B atom = 4.
 - (3) 100% of TVs are occupied by B atoms
 - (4) 50% of TVs are occupied by B atoms.
- 53. An excess of potassium ions makes KCl crystals appear violet or lilac in colour since.....
 - (1) Some of the anionic sites are occupied by an unpaired electron

- (2) Some of the anionic sites are occupied by a pair electrons
- (3) There are vacancies at some anionic sites
- (4) F-centres are created which impart colour to the crystals
- 54. The correct statement(s) regarding defects in solids (are):
 - (1) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion
 - (2) Frenkel defect is a dislocation defect
 - (3) Trapping of an electron in the lattice leads to the formation of F-centre
 - (4) Schottky defects have no effect on the physical properties of solids.
- 55. The correct statement(s) for alkali halides is/are:
 - (1) Metal excess defects make NaCl yellow.
 - (2) Metal excess defects make LiCl, NaCl and KQ coloured.
 - (3) Metal excess defects make NaCl yellow but has in effect on LiCl
 - (4) Metal excess defects make both NaCl and KCl coloured.
- **56.** Which of the following is/are correct about the point defects?
 - (1) In frenkel defect, the dielectric constant of solid increases
 - (2) In Schottky defect, the density of solid decreases
 - (3) In Frenkel defect, the density of solid decreases
 - (4) In Schottky defect, the dielectric constant of solid increases
- 57. Which of the following statements are correct?
 - (1) Ferrimagnetic substances lose ferrimagnetism theating and become paramagnetic.
 - (2) Ferrimagnetic substances do not lose ferrimagnetism on heating and remain ferrimagnetic.
 - (3) Antiferromagnetic substances have domain structures similar to ferromagnetic substances and their magnetic moments are not cancelled by each other.
 - (4) In ferromagnetic substances, all the domains get oriented in the direction of magnetic field and remain as such even after removing the magnetic field.
- **58.** Superconductors are technologically and commercially important substances. The correct information(s) about such conductors are:
 - (1) Phenomena of superconductivity was first discovered by Kammerlingh and Onnes
 - (2) Mercury acts as superconductor at 4 K
 - (3) Superconductors offer zero resistance at zero kelvin
 - (4) Gallium acts as superconductor at 4 K

Linked Comprehension Type



The "OLIVINE" series of minerals consists of crystals in which Fe²⁺ and Mg²⁺ ions may substitute for each other causing substitutional impurity defects without changing the volume of unit cell. In "OLIVINE" series of minerals, O²⁻ ions exist as fcc with Si⁴⁺ occupying one-fourth of OVs and divalent metal ions occupying one-fourth of TVs. The density of "forsterite" (magnesium silicate) is 3.21 g cm⁻³ and that of "fayalite" (ferrous silicate) is 4.34 g cm⁻³.

- 1. The formula of "fayalite mineral" is:
 - (1) Fe₂SiO₄
- (2) FeSiO₄
- (3) Fe₂SiO₆
- (4) FeSiO₃
- 2. If in "forsterite mineral" bivalent Mg²⁺ ions are to be replaced by unipositive Na[®] ions, and if Na[®] ions are occupying half of TVs in fcc lattice, the arrangement of rest of the constituents is kept same, then the formula of the new solid is:
 - (1) Na₂SiO₄
- (2) Na₂SiO₃
- (3) Na₄SiO₄
- $(4) \text{Na}_2 \text{Si}_2 \text{O}_6$
- 3. The percentage of "fayalite" in an "OLIVINE" with density 3.88 g cm⁻³ approximately is:
 - (1) 75%

(2) 59%

(3)35%

(4) 29%

Paragraph 2

AX, AY, BX, and BY have rock salt type structure with following internuclear distances:

Salt	Anion-anion distance in Å	Cation-anion distance in Å
AX	2.40	1.70
AY 1.63		1.15
BX	2.66	1.88
BY	2.09	1.48

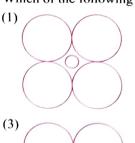
- 4. Ionic radii of A^{\oplus} and B^{\oplus} , respectively, are
 - (1) 0.35 and 0.68 Å
- (2) 0.68 and 0.35 Å
- (3) 1.20 and 0.80 Å
- (4) 0.80 and 1.20 Å
- 5. Ionic radii of X^{\odot} and Y^{\odot} , respectively, are
 - (1) 0.35 and 0.68 Å
- (2) 0.68 and 0.35 Å
- (3) 1.20 and 0.80 Å
- (4) 0.80 and 1.20 Å
- 6. The structure given below is of

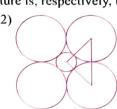


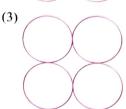
(1) AX

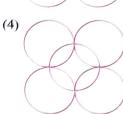
- (2) AY, BX
- (3) AY, BX, BY
- (4) AY, BX, BY, and KCl

7. Which of the following structure is, respectively, by AX?









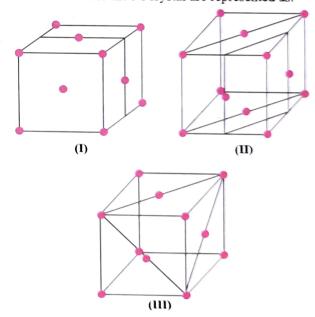
- 8. A salt MY crystallizes in the CsCl structure. The anions at the corners touch each other and cation is in the centre. The radius ratio (r_{\oplus}/r_{\ominus}) for this structure is
 - (1) 0.225

(2) 0.414

- (3) 0.732
- (4) 1.0

Paragraph 3

The length of a unit cell (a) in the Ni crystal is 0.352 nm. The diffraction of X-rays of 0.154 nm wavelength (λ) from a Ni crystal occurs at 22.2°, 25.9°, and 38.2°. By using Bragg's law, ($n\lambda = 2d \sin \theta$), and assuming that the diffractions are first order (n = 1), the distances are calculated to be 0.204 nm, 0.176 nm and 0.124 nm. The various structures for the Ni crystal are represented as:



- **9.** The distance (*d*) of 0.204 nm represent which structure?
 - (1)I

(2) 11

(3) III

- (4) All
- **10.** The distance (*d*) of 0.176 nm represent which structure?
 - (1)I

(2) II

(3) III

- (4) None
- 11. The distance (d) of 0.124 nm represent which structure?
 - (1)I

- (2) II
- (3) III
- (4) All

- 12. Which of the following statements is correct?
 - (1) I represents sc-type structure
 - (2) II represents bcc-type structure
 - (3) III represents both sc- and bcc-type structure.
 - (4) All figures represent fcc-type structure.

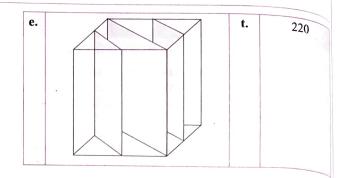
Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

1.	Column I Elements of symmetry (For a cube)			Column II Ions touched (In NaCl structure)				
	a. Body diagonal		p.	Only 2 face centre ions				
	b.	C ₄ axis (tetrad axis)	q.	Only 2 corners ions				
	c.	c. Rectangular plane		Body centre ion				
	- 63		s.	Only one octahedral void				

	Column I		Column II					
a.	F-centres	p.	Extra cations present in interstitial sites					
b.	Metal excess defect	q.	Some cations are replaced by one of higher valence					
c.	Metal deficiency defect	r.	Both cations and anions are missing from lattices					
d.	Schottky defects	s.	Electrons trapped in anionic vacancies					

	Column I	C	olumn II
	Type of crystal structure	Тур	e of plane
a.		p.	101
b.		q.	110
c.		r.	022
d.		S.	101



4.		Column I		Column II			
	Compounds		Name of structure				
	a.	Fe ^{III} (Fe ^{II} Fe ^{III})O ₄	p.	Rutile structure			
	b.	$Mg^{II}Al_2^{\ III}O_4$ and $Co^{II}(Co^{III})_2O_4$	q.	Inverse 2 : 3 spinel structure			
	c.	MnO ₂ and SnO ₂	r.	Normal 2: 3 spinel structure			
	d.	BaTiO ₃	s.	Perovskite structure			
	e.	CaF ₂ and SrCl ₂	t.	Fluorite-type structure			

Column I			Column II
a.	Even value of $h + k + l$	p.	AgBr
b.	Substances having both Schottky and Frenkel defects	q.	Insulator
c.	Devices that convert electrical energy to mechanical strain and vice versa	r.	bcc structure
d.	Materials having conductivity range 10^{-10} – 10^{-20} S m ⁻¹	s.	Piezoelectric crystal
e.	Substances having a rutile structure	t.	NaCl
f.	Substance having Schottky defects	u.	Coordination number 6:3

	Column I		Column II			
	Types of crystal	Location of cations/anic				
a.	Na ₂ O	p.	Anions = fcc Cations = Alternate TVs			
b.	CaF ₂	q.	Anions = fcc Cations = All TVs			
c.	ZnS	r.	Cations = fcc Anions = All TVs			
d.	NaCl	s.	Anions = fcc Cation = $\frac{1}{8}$ TVs + $\frac{1}{2}$ OV			
е.	Spinel (MgAl ₂ O ₄)	t.	Anions = hcp Cations = $2/3$ of OVs			
f.	Corundum	u.	Anions = fcc Cations = All OVs			

For Q.7 to Q10: Answer the question given below by appropriately matching the information given in three column of the following table

	Column I	131031	Column II		Column III
	Statement		Characteristics (I)		Characteristics (II)
a	In the FCC unit cell, two voids are formed on each non parallel body diagonal of the cube	ì	All octahedral voids are empty	р	Coordination number = 4:4
b	In the FCC unit cell voids are formed at the body centre of the cube and on edge centre	ii	4 void / unit cell	q	Nearest distance between two atoms = $\frac{\sqrt{3}}{4}$ a
c	FCC structure with 4 more atoms that are present in the alternate tetrahedral voids	iii	8 void / unit cell	r	Nearest distance between two voids = $\frac{a}{\sqrt{2}}$
d	CCP arrangement in which A ²⁻ ion form FCC and each B ²⁺ ion is surrounded tetrahedrally by A ²⁻ ions and vice versa. B ²⁺ ions are in alternate tetrahedral voids	iv	Packing efficiency = 34%	S	Nearest distance between two voids = $\frac{1}{2}$ × Body diagonal
	nord one armos of the color of the arms and the color of			t	Nearest distance between two voids = $\frac{\sqrt{3}}{2}$ a

- 7. Which of the following combination correctly represents the Tetrahedral voids?
 - (1) a—iii—s, t
- (2) a—iii—s
- (3) b—iii—i
- (4) b—ii—p
- **8.** Which of the following combination correctly represents the Octahedral voids?
 - (1) a—iii—s
- (2) b—ii—s
- (3) c—iv—q
- (4) b—ii—r
- 9. Which of the following combination correctly represents the structure of "diamond cubic"?
 - (1) a—iii—t
- (2) c—iv—q
- (3) c—iv—r
- (4) d-i-p
- 10. Which of the following combination represents crystal structure of Sphalerite type?
 - (1) a—i—p
- (2) b—ii—r
- (3) d-i-p
- (4) d—i—r

Numerical Value Type



- 1. If a solid $A^{\oplus}B^{\ominus}$ having ZnS structure is heated so that the ions along two of the axis passing through the face centre particles are lost and bivalent ion (Z) enters here to maintain the electrical neutrality, so that the new formula unit becomes $A_x B_y Z_c$, report the value of x + y + c.
- 2. Metal M of radius 50 nm is crystallized in fcc type and made cubical crystal such that face of unit cells aligned with face of cubical crystal. If the total number of metal atoms of M

at all faces of cubical crystal is 6×10^{30} , then the area of one face of cubical crystal is $A \times 10^{16}$ m². Find the value of A.

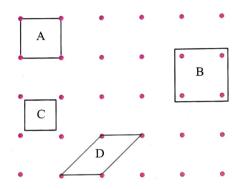
- 3. O^{2-} ions are arranged in ccp in a spinel structure. A^{2+} ions occupy 1/8 of TVs and B^{\oplus} ions occupy half of OV. The void volume of unit cell = 0.11 A. Find the value of A.
- **4.** Find the coordination number of Na^{\oplus} in Na_2O .
- 5. A bcc lattice is made up of hollow spheres of B. Spheres of solids A are present in hollow spheres of B. The radius of A is half of the radius of B. The ratio of total volume of spheres of B unoccupied by A in a unit cell and volume of unit cell is $A \times \frac{\pi\sqrt{3}}{64}$. Find the value of A.
- **6.** Give the total score of the correct statements of the following.

4 70	Statements	Score
a.	In an antifluorite structure, cations are present in all TVs.	l
b.	If the radius of cation is 0.35 pm and that of anion is 0.95 pm, then the CN of the crystal is 4.	2
c.	An atom or ion is transferred from a lattice site to an interstitial position in Frenkel defect.	3
d.	The density of a crystal always decreases in point defects.	4

7. Give the total score of the correct statements of the following.

State	ements	Score
a.	First two nearest neighbour distances for sc lattice are, respectively, a and $\sqrt{2}a$.	4
b.	First two nearest neighbour distances for bcc lattice are, respectively, $\frac{\sqrt{3}a}{2}$ and a.	3
c.	In ZnS (wurtzite), Zn ²⁺ ions occupy lattice point while in ZnS (zinc blende), Zn ²⁺ ions occupy alternate TVs.	2
d.	In point defects, volume and geometry of the crystal do not change.	1

8. In the figure given below, four parallelograms are shown. How many parallelograms are unit cells?

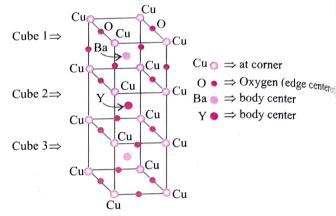


9. Caesium atoms are the largest naturally occurring alon The radius of Cs atom is 2.6 Å. The number of $m_{0|e_1}$ Cs atoms to be laid side by side to give a row of C_8 \mathfrak{al}_{f_0} 2.50 cm long is $x \times 10^{-17}$. Find the value of x.

Note: For Q.10, the integer value is between 10 and 20

10. The following figure shows the unit cell of a compound, a mixed oxide of yttrium, barium, and copper. The form of mixed oxide is Y_aBa_bCu_cO_d.

Find the value of (a + b + c + d).



11. A solid has a structure in which X atoms are located at culcorners of unit cell, O atom are at the edge centres and atoms at cube centre.

Then the formula of compound is $X_a Y_b O_c$. If two atoms of O are missing from any of two edge centre per unit cell, then the molecular formula is X,Y,O, Then, find the value of (x + y + z) - (a + b + c).

Archives

JEE MAIN

Single Correct Answer Type

- 1. Copper crystallises in fcc with a cell length of 361 pm. What is the radius of copper atom?
 - (1) 127 pm
- (2) 157 pm
- (3) 181 pm
- (4) 108 pm

(AIEEE 2009)

- 2. Percentage of free space in cubic close packed structure and in body centred structure are respectively:
 - (1) 48% and 26%
- (2) 30% and 26%
- (3) 26% and 32%
- (4) 32% and 48%

(AIEEE 2010)

- 3. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is:
 - (1) 144 pm
- (2) 288 pm
- (3) 398 pm
- (4) 618 pm
- (AIEEE 2010)
- 4. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centred positions. If one atom of B missing from one of the face centred points, the formula of the compound is:
 - (1) A_2B
- (2) AB₂
- $(3) A_2B_3$
- $(4) A_2B_5$
- (AIEEE 2011)

- 5. Lithium forms body centred cube structure. The length of side of its unit cell is 351 pm. Atomic radius of the limit will be
 - (1) 300 pm
- (2) 240 pm
- (3) 152 pm
- (4) 75 pm
- 6. Which of the following exists as covalent crystals in solid state?
 - (1) Sulphur
- (2) Phosphorus
- (3) Iodine
- (4) Silicon (JEE Main 2015

(AIEEE 201)

- 7. Experimentally it was found that a metal oxide has form $M_{0.98}O_1$. Metal M, is present as M^{2+} and M^{3+} in its fraction of the metal which exists as M3+ would be.
 - (1) 6.05%

correct?

- (2) 5.08%
- (3) 7.01%
- (4) 4.08%
- (JEE Main 2015 8. CsCl crystallises in body centred cubic lattice. If 'a' is edge length then which of the following expressions
 - (1) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{a\sqrt{3}}{2}$ (2) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = a\sqrt{3}$

 - (3) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 3a$ (4) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{3a}{2}$

(JEE Main ²⁰¹

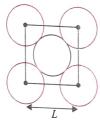
- 9. Sodium metal crystallizes in a body-centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately:
 - (1) 1.86 Å
- (2) 3.22 Å
- (3) 5.72 Å
- (4) 0.93 Å (JEE Main 2015)
- 10. Which of the following compounds is metallic and ferromagnetic?
 - (1) MnO₂
- (2) TiO₂
- (3) CrO₂
- (4) VO,
- (JEE Main 2016)
- 11. A metal crystallizes in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be:
 - (1) 2a
- (2) $2\sqrt{2} a$
- (3) $\sqrt{2} \ a$
- (4) $\frac{a}{\sqrt{2}}$ (JEE Main 2017)
- 12. Which type of 'defect' has the presence of cations in the interstitial sites?
 - (1) Vacancy defect
 - (2) Frenkel defect
 - (3) Metal deficiency defect
 - (4) Schottky defect

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

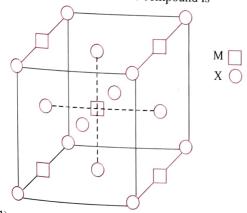
1. The packing efficiency of a two-dimensional square unit cell shown below is



- (1) 39.27%
- (2) 68.02%
- (3) 74.05%
- (4) 78.54%

(IIT-JEE, 2010)

2. A compound $M_p X_q$ has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is



- (1) MX
- (2) MX_{2}
- (3) M_2X
- $(4) M_5 X_{14}$

(IIT-JEE-2012)

- 3. Experimentally it was found that a metal oxide has formula $M_{0.98}$ O. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M³⁺ would be:
 - (1) 4.08%
- (2) 6.05%
- (3) 5.08%
- (4) 7.01%

(JEE Advanced, 2013)

- 4. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminum ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n, respectively,
- (2) $1, \frac{1}{4}$
- (4) $\frac{1}{4}, \frac{1}{8}$

(JEE Advanced, 2015)

Multiple Correct Answers Type

- 1. Which of the following statements regarding defects in solids is/are correct?
 - (1) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.
 - (2) Frenkel defect is a dislocation defect.
 - (3) Trapping of an electron in the lattice leads to the formation of F-centre.
 - (4) Schottky defects have no effect on the physical properties of solids. (IIT-JEE 2009)
- 2. The CORRECT statement(s) for cubic close packed (ccp) three dimensional structure is(are)
 - (1) The number of the neighbours of an atom present in the topmost layer is 12.
 - (2) The efficiency of atom packing is 74%.
 - (3) The number of octahedral and tetrahedral voids per atom are 1 and 2 respectively.
 - (4) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom. (JEE Advanced, 2016)

Numerical Value Type

- 1. Find the number of hexagonal faces that are present in a truncated octahedral. (IIT-JEE 2011)
- 2. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm⁻³, then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value (JEE Advanced 2017)
- 3. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance.
 - (i) Remove all the anions (X) except the central one
 - (ii) Replace all the face centered cations (M) by anions (X)
 - (iii) Remove all the corner cations (M)
 - (iv) Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in Z is _____.

Answers Key

EXERCISES

Single Co	rrect Answei	Туре		
1.(2)	2. (4)	3. (2)	4. (1)	5. (3)
6. (4)	7. (2)	8. (2)	9. (1)	10. (4)
11.(3)	12. (3)	13. (2)	14. (2)	15. (3)
16. (4)	17. (1)	18. (3)	19. (3)	20. (4)
21. (2)	22. (2)	23. (4)	24. (1)	25. (2)
26. (2)	27. (2)	28. (1)	29. (2)	30.(2)
31. (3)	32. (2)	33. (4)	34. (3)	35. (3)
36. (4)	37. (4)	38. (2)	39. (2)	40. (3)
41.(2)	42. (1)	43. (1)	44. (2)	45. (1)
46. (2)	47. (2)	48. (2)	49. (2)	50. (1)
51. (1)	52. (1)	53. (2)	54. (1)	55. (3)
56. (4)	57. (2)	58. (2)	59. (3)	60.(2)
61. (4)	62. (2)	63. (1)	64. (1)	65. (3)
66. (2)	67. (4)	68. (2)	69. (2)	70. (1)
71. (3)	72. (4)	73. (2)	74. (1)	75. (3)
76. (3)	77. (3)	78. (3)	79. (4)	80. (3)
81. (1)	82. (2)	83. (4)	84. (2)	85. (4)
86. (4)	87. (2)	88. (4)	89. (2)	90. (4)
91. (2)	92. (1)	93. (2)	94. (1)	95. (3)
96. (2)	97. (3)	98. (2)	99. (2)	100. (3)
101. (1)	102. (2)	103. (4)	104. (2)	105. (2)
106. (3)	107. (3)	108. (4)	109. (2)	110. (2)
111. (4)	112. (1)	113. (1)	114. (3)	115. (2)
116. (4)	117. (1)	118. (3)	119. (2)	120. (3)
121. (4)	122. (3)	123. (2)	124. (2)	125. (2)
126. (4)	127. (3)	128. (1)	129. (2)	130. (3)
131. (2)	132. (2)	133. (2)	134. (1)	135. (3)
36. (2)	137. (1)	138. (2)	139. (3)	140. (2)
41. (1)	142. (1)	143. (1)	144. (2)	145. (1)
46. (2) 51. (1. 2	147. (2)	148. (2)	149. (1)	150. (2)
51. (1, 3, 52, (1, 2)		152. (1, 2,		15((0)
53. (1, 2, 57. (2)		154. (3) 159. (2)	155. (2)	156. (2)
31. (2)	158. (1)	137. (2)	160. (3)	161. (3)

Multiple Correct Answers Type

163.(1)

162. (2)

1. (1, 3)	2. (1, 4)	3. (3, 4)
4. (1, 2, 4)	5. (1, 3)	6. (2, 4)
7. (1, 4)	8. (1, 2, 3)	9. (1, 2, 3, 4)
10. (1, 2, 3)	11. (1, 2)	12. (1, 2, 3, 4)
13. (1, 2, 3, 4)	14. (2, 3)	15. (1, 3)
16. (1, 4)	17. (1, 2, 4)	18. (1, 2, 4)
19. (1, 2, 3, 4)	20. (1, 2, 3)	21. (1, 2, 3)
22. (2, 4)	23. (2)	24. (1, 2, 3, 4)
25. (1, 3)	26. (3, 4)	27. (2, 3, 4)
28. (1, 4)	29. (1, 2, 4)	30. (2, 3)
31. (1, 3, 4)	32. (1, 2, 3, 4)	33. (1, 2)
34. (2, 3)	35. (1, 2, 3)	36. (1, 2, 3, 4)

164. (4)

165. (1)

37. (1, 3)	38. (1, 2, 3)	39. (3, 4)
40. (2, 3)	41. (1, 2, 3)	42. (1, 2, 3)
43. (1, 2, 3, 4)	44. (1, 2, 3, 4)	45. (2, 3, 4)
46. (1, 2, 3, 4)	47. (1, 2, 3, 4)	48. (1, 2, 4)
49. (1, 2, 3, 4)	50. (1, 3, 4)	51. (1, 2, 3, 4)
52. (1, 2, 3)	53. (1, 4)	54. (2, 3)
55. (1, 2, 4)	56. (1, 2)	57. (1, 4)
58. (1, 2, 3)		

Linked Comprehension Type

1. (1)	2. (3)	3. (2)	4. (1)	5. (3)
6. (4)	7. (1)	8. (3)	9. (3)	10. (1)
11. (2)	12. (4)			(1)

Matrix Match Type

Q. No.	a	b	c	d	e	f	g
1.	q, r, s	p, r, s	r	_		_	-
2.	S	р	q	r		_	
3.	q	p	S	r	t	_	
4.	q	r	p	S	t	_	_
5.	r	p	S	q	u	t	
6.	q	r	p	u	S	t	

7. (1) 8. (4) 9. (2)	10. (4)
---	----------------

Numerical Value Type

1. (7)	2. (2)	3. (2)	4. (4)	5. (7)
6. (6) 11. (4)	7. (8)	8. (2)	9. (8)	10. (13)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (1)	2. (3)	3. (1)	4. (4)	5. (3)
6. (4)	7. (4)	8. (1)	9. (1)	10.(3)
11. (4)	12. (2)		(-)	

JEE Advanced

Single Correct Answer Type

1.	(4)	2. (2)	3 (1)	4 (1)
	(T)	4. (2)	3. (1)	4. (1)

Multiple Correct Answers Type

1. (2, 3) **2.** (2, 3, 4)

Numerical Value Type

1. (8)	2. (2)	3. (3)
1. (8)	2. (2)	3. (3)

OVERVIEW

 Solution: A homogeneous mixture of two or more components whose concentration can be varied within a limit.

Alternatively, a mixture of solute and solvent is called solution.

2. Solubility: The amount of solute which can be dissolved in 100 g of a solvent is called its solubility to make a saturated solution.

If the hydration energy is greater than the lattice energy, then the solute is soluble in solution and energy is released, i.e., ΔH solution is negative.

3. Vapour pressure of liquid: At a given temperature, the pressure exerted by the vapours when they are is equilibrium with the liquid is called the vapour pressure of the liquid.

Greater the force of attraction between liquid molecules, lower is the vapour pressure and vice versa.

4. Vapour pressure of a solution: A solution is formed when a miscible solute is added to a pure solvent. Some solute molecules replace the molecules of solvent from the surface. Therefore, the escaping tendency of the solvent molecules decreases, which causes lowering in the vapour pressure of solution, that is, $p_{\text{solution}} < p^{\circ}$

5. a. Raoult's law

When two miscible volatile liquids are heated, the partial pressure of one component is equal to the product of the mole fraction and pure pressure of that component. Alternatively, the partial pressure of each component in the solution is directly proportional to its mole fraction. $P_{\text{total}} \propto \chi_{\text{A}} \text{ or } \chi_{\text{B}}$

- **b.** If only solvent component (A) is volatile, then the vapour pressure of solution is $p_S = P_A^{\circ} \chi_A$.
- c. Mole fraction of solvent (A) in vapour phase,

$$\chi_{\rm A}^{\rm V} = \frac{p_{\rm A}}{P_{\rm total}}$$

6. Ideal solution: They obey Raoult's law for all ranges of concentration and temperature. In these solutions solute–solute and solvent–solvent interactions are almost similar to solute–solvent interactions. Substances having similar structures and polarities form nearly ideal solutions, e.g., $C_2H_5Br + C_2H_5I$.

A-A or B-B interaction = A-B interaction

$$\Delta_{\text{mix}}H=0$$

$$\Delta_{\text{mix}} V = 0$$

7. Non-ideal solutions

They do not obey Raoult's law at any concentration. These are solutions in which solute-solute and solvent-solvent interactions are different than solute-solvent interactions.

A–A or B–B interaction ≠ A–B interaction.

$$\Delta_{\text{mix}} H \neq 0$$

$$\Delta_{\min} V \neq 0$$

There are two types of such solutions:

a. Solutions which show positive deviations from ideal solution if A-A or B-B interaction > A-B interaction.

$$\Delta_{\text{mix}}H > 0$$
 and $\Delta_{\text{mix}}V > 0$

b. Solutions which show negative deviation from ideal solution if A-A or B-B interaction < A-B interaction.

$$\Delta_{\text{mix}} H < 0$$
 and $\Delta_{\text{mix}} V < 0$

8. Henry's law: (solubility of a gas in liquid): At constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas. The solubility of gases increases with increase of pressure and decreases with increase of temperature. Henry's law states that "the partial pressure of the gas in the vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution" and is expressed as:

$$p = K_{\rm H} \chi$$

where $K_{\rm H}$ is Henry's law constant and χ is the mole fraction of solute.

- 9. Azeotropic or constant boiling mixtures: A liquid mixture having a definite composition and boiling like a pure liquid is called a *constant boiling mixture* or an azeotropic mixture or simply an azeotrope. Azeotropic mixtures are of two types:
 - a. Minimum boiling azeotropes: The boiling point of an azeotrope is less than the boiling point of either of the pure components.
 - b. Maximum boiling azeotropes: The boiling point of an azeotrope is higher than that of either of the pure components.

Azeotropic mixtures cannot be separated into their constituents by fractional distillation.

- 10. Colligative properties: Certain properties of ideal solutions depend only on the number of particles of the solute in a definite amount of the solvent and do not depend on the nature of solute. Such properties are called colligative properties.
- 11. Relative lowering of vapour pressure

$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \chi_{B} = \frac{n_{B}}{n_{A} + n_{B}}$$

where P° = Vapour pressure of pure solvent

 P_s = Vapour pressure of solution

 χ_B = Mole fraction of solute

 n_A , n_B = Moles of solvent and solute

In terms of molecular weight of solute

$$Mw_{\rm B} = \frac{W_{\rm B} \times Mw_{\rm A}}{W_{\rm A} \left(\frac{P_{\rm A} \circ - P_{\rm s}}{P^{\circ}}\right)}$$

$$\frac{P^{\circ} - P_{S}}{P_{S}} = \frac{n_{B}}{n_{A}}$$
 (for all kinds of solutions)

$$\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} = \frac{n_{\rm B}}{n_{\rm A}}$$
 (for dilute solutions)

12. Osmosis: The net spontaneous flow of the solvent molecule from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semipermeable membrane is called osmosis.

Osmotic pressure
$$(\pi) = CRT = \frac{n}{V}RT$$

In term of molecular weight

$$\pi = \frac{W_{\rm B}RT}{V\ Mw_{\rm B}}$$
 or $Mw_{\rm B} = \frac{W_{\rm B}RT}{V\pi}$

- 13. Isotonic solutions: Solutions having same osmotic pressure are called isotonic or isomotic solutions. A pure solution of 0.91% NaCl is isotonic with human red blood cells (RBCs). Therefore, in this solution RBCs neither swell nor undergo plasmolysis. The shrinking of cell due to the flow of water out of the cell is called plasmolysis or crenation.
- 14. Hypertonic solutions: The solution which has higher osmotic pressure than any other solution is called hypertonic solution.

A pure NaCl solution with concentration more than 0.91% is called hypertonic solution. On placing RBCs in this solution. they shrink due to plasmolysis.

15. Hypotonic solutions: The solution which has lower osmotic pressure than some other solution is called hypotonic solution. A pure NaCl solution with concentration less than 0.91% is called hypotonic solution. On placing RBCs in this solution, they will swell and even burst. The process of swelling of the cell resulting into rupturing of the cell is known as hemolysis.

16. Elevation in boiling point (ΔT_b)

$$\Delta T_b = K_b m; \quad K_b = \text{molal elevation constant}$$

$$m = \text{molality}$$

$$=\frac{K_{\rm b}\times 1000\times W_{\rm B}}{W_{\rm A}\times Mw_{\rm B}}$$

$$\therefore K_{\rm b} = \frac{Mw_{\rm A}RT_{\rm b}^2}{\Delta_{\rm van}H \times 1000} \text{ or } \frac{RT_{\rm b}^2}{l_{\rm v} \times 1000}$$

 $\Delta_{\text{vap}} H = \text{Enthalpy of vapourization}$

$$l_{\rm v}$$
 = Latent heat of vapourization = $\left(\frac{\Delta_{\rm vap}H}{Mw_{\rm solvent}}\right)$

Molal elevation constant (K_b) may be defined as the elevation in boiling point when the molality of the solution is unit Unit of K_h is K m⁻¹ or °C m⁻¹ or K kg mol⁻¹.

17. Depression in freezing point (ΔT_c)

 $\Delta T_{\rm f} = T_{\rm 0} - T_{\rm s} = K_{\rm f} \times m$; where $K_{\rm f}$ is molal depression constant or cryoscopic constant.

or
$$\Delta T_{\rm f} = \frac{K_{\rm f} \times 1000 \times W_{\rm B}}{W_{\rm A} \times M w_{\rm B}}$$

$$= \frac{M w_{\rm A} \times R T_{\rm f}^2}{\Delta_{\rm fus} H \times 1000} \quad \text{or} \quad \frac{R T_{\rm f}^2}{l_{\rm f} \times 1000}$$

$$l_{\rm f} = {\rm latent\ heat\ of\ fusion} = \frac{\Delta_{\rm fus} H}{M w_{\rm solvent}}$$

Unit of K_f is K m⁻¹ or °C m⁻¹ or K kg mol⁻¹.

- 18. Molecular masses of macromolecules (i.e., polymers and proteins) are determined by osmotic pressure method because other colligative properties give so low values while are difficult to measure. Moreover, these methods requi heating which changes their properties (e.g., proteins coagulated on heating).
- **19.** All colligative properties $\left(\text{e.g.,} \frac{\Delta P}{D^{\circ}}, \Delta T_{\text{b}}, \Delta T_{\text{f}}, \text{ and } \pi\right)^{\text{at}}$ directly proportional to the number of moles of soluto But freezing point and vapour pressure of the solution

Number of moles of solutes

- 20. Relationship between different colligative properties
 - **a.** Osmotic pressure (π) with relative lowering of vapou pressure:

$$\pi = \frac{P^{\circ} - P_{S}}{P^{\circ}} \times \frac{dRT}{Mw_{B}}$$

$$\begin{bmatrix} d = \text{density of the solution} \\ Mw_{\text{B}} = \text{Molecular mass of solution} \end{bmatrix}$$

b. Osmotic pressure (π) with depression in boiling point

$$\pi = \Delta T_{\rm b} \times \frac{dRT}{1000K_{\rm b}}$$

Osmotic pressure (π) with depression in freezing point (ΔT_{ϵ}) :

$$\pi = \Delta T_{\rm f} \times \frac{dRT}{1000K_{\rm f}}$$

d. Elevation in boiling point with relative lowering of vapour pressure:

$$\Delta T_{\rm b} = \frac{1000 \, K_{\rm b}}{M w_{\rm A}} \left(\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} \right)$$

$$\begin{bmatrix} M w_{\rm A} = \text{Molecular mass} \\ \text{of solvent} \end{bmatrix}$$

e. Depression in freezing point with relative lowering of vapour pressure:

$$\Delta T_{\rm f} = \frac{1000 \ K_{\rm f}}{M w_{\rm A}} \left(\frac{P^{\rm o} - P_{\rm S}}{P^{\rm o}} \right)$$

21. Van't Hoff factor (i)

$$i$$
= $\frac{\text{Observed colligative property}}{\text{Normal colligative property}}$

$$= \frac{\text{Normal (calculated) molecular mass}}{\text{Abnormal (observed) molecular mass}} = \frac{Mw_{(c)}}{Mw_{(o)}}$$

For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows:

$$\Delta T_{b} = iK_{b}m$$

$$\Delta T_{f} = iK_{f}m$$

$$\frac{\Delta P}{P^{o}} = i\chi_{\text{solute}}$$

$$\pi = iCRT$$

22. van't Hoff factor, i > 1, if there is dissociation of the solute in the solution and i < 1 if there is association of the solute in the solution.

For 100% dissociation of a solute, i = number of ionsproduced from one molecule of the solute.

- ⇒ If observed colligative property < calculated value or $Mw_{(0)} < Mw_{(c)}$ (or i < 1), there is association.
- ⇒ If observed colligative property > calculated value or $Mw_{(0)} < Mw_{(c)}$ (or i > 1), there is dissociation.

INTRODUCTION

A solution is a homogeneous mixture of two or more than two components dispersed on a molecular scale. A solution depending upon the number of components can be classified as binary solution (two components), ternary solution (three components), quaternary solution (four components), and so on. In solution the component which is present in excess amount is called the solvent and the component which is present in lesser amount is called as solute. In other words a solute is a substance that dissolves while solvent is a substance in which dissolution takes place. A solution is a single-phase system and the components may be in solid, liquid, or gaseous state, and therefore, different types of solutions are possible and summarized in Table 2.1.

Table 2.1 Different types of solutions

Type of solutions	Common example
Gaseous solution	All the second s
Gas in gas Liquid in gas	A mixture of oxygen and nitrogen gases Chloroform vapours mixed with nitrogen gas
Solid in gas	Camphor vapours in nitrogen gas
Liquid solution Gas in liquid Liquid in liquid Solid in liquid	Oxygen dissolved in water Ethanol dissolved in water Sucrose dissolved in water
Solid solution Gas in solid Liquid in solid Solid in solid	Solution of hydrogen in palladium Amalgam of mercury with sodium Copper dissolved in gold

2.2 TYPES OF SOLUTION

2.2.1 SOLID SOLUTION

Solid in Solid

This type of solution is formed by mixing two solid components. For example, brass bronze, monel metal, and steel.

Solid solutions are classified into two categories: substitutional solid solutions and interstitial solid solutions.

(a) Substitutional solid solutions are formed by placing atoms of one kind into the place of other substance in its crystal lattice as shown in Fig. 2.1. Brass is a common example of the substitutional solid solution of copper and zinc.

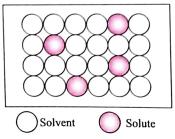


Fig. 2.1 Substitution solid solution

(b) Interstitial solid solutions are formed by placing atoms of other in the lettice of atoms of other in kind into the voids in the lattice of atoms of other substance as shown in Fig. 2.2. Tungsten carbide, an extremely have as snown in 1.8. substance, is a common example of interstitial solid solutions

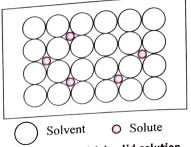


Fig. 2.2 Interstitial solid solution

Solutions of Solids in Liquid

The solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid (solute) in grams which can dissolve in 100 g of the liquid (solvent) to form a saturated solution at that particular temperature.

Following are the factors affecting the solubility of a solid in a liquid.

(a) Nature of the solute and solvent

In general, a solid dissolves in a liquid which is chemically similar to it. It can be also said as "like dissolves like", i.e., an ionic compound or polar compound dissolves in a polar solvents whereas non-polar compounds dissolve in nonpolar solvents.

For example, common salt (an ionic compound) is more soluble in water (a polar solvent). Similarly, non-polar (i.e., covalent or organic) iodine is more soluble in alcohol a carbon tetrachloride (covalent liquids).

The reason for the solubility of an ionic compound in polar solvent is because of strong electrostatic forces of attraction between the ions of the crystal and the polar solvenia molecules, the negative ions being attracted by the positive poles of the solvent molecules and the positive ions by the negative poles of the solvent molecules. For example when water is used as the solvent (Fig. 2.3), the water molecule pull the ions of the crystal apart and the electrostatic force of attraction existing between the ions are surrounded by the water molecules which act as an envelope around the ions and prevent the recombination of ions. The ions thus moving freely in the solution are said to be hydrated It may be mentioned here that whereas energy is required for the splitting of the ionic compound into ions (called lattice energy), energy is given out when the ions get hydrated (called hydration energy). A substance dissolves if theft is not evolution of energy, i.e., lowering of energy occurs which will happen if hydration energy is greater than the lattice energy.

The other polar solvents are liquid ammonia, liquid hydrogen sulphide, and liquid sulphur dioxide which are also good solvents for ionic compounds.

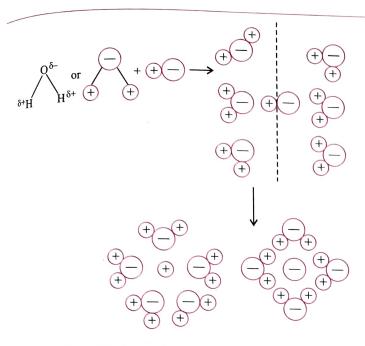


Fig. 2.3 Dissolution of an ionic compound in a polar solvent water (H₂O)

The solubility of non-polar compounds is due to similar solute-solute, solute-solvent, and solvent-solvent interactions.

(b) Effect of temperature on solubility: Solubility curve

Various ionic substances can be classified into three categories based on the effect of temperature on solubility in water.

- (i) Ionic substances whose solubility decreases continuously with increase of temperature
 - There are a few substances such as cerium sulphate, lithium carbonate, sodium carbonate monohydrate (Na₂CO₃·H₂O), etc., whose solubility decreases with increase of temperature.
- (ii) Ionic substances whose solubility increases continuously with increase of temperature
 - Most of the substances such as NaNO₃, KNO₃, NaCl KCl, etc., fall in this category. The reason for this behaviour is that in case of all such substances, the process of dissolution is endothermic, i.e.,

on applying Le Chatelier's principle, as the temperature is increased, equilibrium will shift in a direction in which the heat is absorbed, i.e., in the forward direction. Consequently, more of the solute passes into the solution.

(iii) Ionic substance whose solubility does not increase or decrease continuously.

There are some substances which on heating change at a particular temperature from one polymorphic form to another (like α to β form as in the case of ammonium nitrate) or from one hydrated form to another (e.g., $CaCl_2 \cdot 6H_2O \longrightarrow CaCl_2 \cdot 4H_2O \longrightarrow CaCl_2 \cdot 2H_2O$) or from hydrated to anhydrous form (e.g., $Na_2SO_4 \cdot 10H_2O \longrightarrow Na_2SO_4$). The temperature at which one form of the substance changes into another is called *transition temperature*.

Such substances do not show a continuous increase or decrease of solubility. For example, the solubility of

sodium sulphate first increases upto 32.4°C and then begins to decrease.

When solubilities are plotted against temperatures, the curve obtained is called *solubility curve*.

2.2.2 GASEOUS SOLUTION

All the gases form a homogeneous mixture and are therefore regarded as solutions. Air is an example of gaseous solutions; more examples are listed in Table 2.1.

2.2.3 LIQUID SOLUTION

Liquid solutions are formed by mixing solids or gases in liquid or liquid in liquid homogeneously. Examples of liquid solutions are listed in Table 2.1.

2.3 METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION AND "n" FACTOR

Refer to overview point (1-14) chapter 1 and overview point (1-30) chapter 3, physical chemistry part 1.

2.4 SOLUBILITY OF A GAS IN A LIQUID

Gases dissolve in liquids to form homogeneous solutions. For example, soda water contains carbon dioxide dissolved in water under high pressure. Oxygen is sufficiently soluble in water to allow the survival of aquatic life in lakes, riversand, and oceans.

The solubility of a gas in a liquid (also called the solubility co-efficient) can be defined as the volume of the gas (in cm³) which will dissolve in 1 cm³ of the liquid to form a saturated solution at particular temperature and pressure.

The solubility of a gas in a liquid is determined by several factors:

- (a) The nature of the gas and the solvent: The solubility of different gases varies considerably in the same solvent. Some gases are more soluble whereas some gases are less soluble, i.e., it depends upon the nature of gas, e.g., oxygen, nitrogen, helium, and argon are less soluble in water whereas sulphur dioxide, hydrogen chloride, and ammonia are more soluble in water because they chemically react with water and form sulphurous acid, hydrochloric acid, and ammonium hydroxide, respectively.
- (b) The effect of temperature: The solubility of a gas decreases with increase in temperature. This is because on heating the solution of a gas some gas is usually expelled out of the solution. This can be understood as follows:

The dissolution of a gas in an exothermic process, i.e., it is accompanied by evolution of heat

Gas + Solvent

Solution + Heat

On applying Le Chatelier's principle, it is evident that the increase in temperature would shift the equilibrium in the backward direction, i.e., the solubility would decrease.

Though generally the solubility of a gas in a liquid decreases with increase in temperature, there are some exceptions. For example, the solubility of some sparingly soluble gases, such

as hydrogen and inert gases, increases slightly with increase of temperature, specially in the non-aqueous solvent such as hydrocarbons, alcohol, and acetone.

(c) Effect of pressure: The solubility of gases increases with increase of pressure.

Henry's law gives a quantitative relationship between the solubility of gas and the pressure. This law states that at a given temperature the mass of dissolved gas in a given volume of solvent is proportional to the pressure of the gas with which it is in equilibrium.

If m is the mass of the gas dissolved by unit volume of the solvent, and the pressure of the gas at equilibrium with solution is P, then according to Henry's law,

$$m \propto P$$
 or $m = K \cdot P$

where K is the proportionality constant and depends upon the nature of gas, nature of solvent, temperature, and units of pressure.

If we plot a graph between the solubility of gas and the equilibrium pressure at a constant temperature, a straight line would be observed (Fig. 2.4).

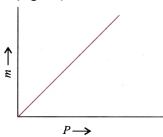


Fig. 2.4 Variation of solubility of gas with pressure

Figure 2.5 shows the variation of solubility of some gases at equilibrium pressure over the solution.

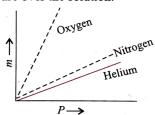


Fig. 2.5 Variation of solubility of some gases with equilibrium pressure

The variation of these gases depends upon their nature. Dalton, a contemporary of Henry, concluded independently that the solubility of a gas in a liquid solution depends upon the partial pressure of the gas.

2.4.1 HENRY'S LAW IN THE FORM OF MOLE FRACTION

According to Henry's law, the mass of gas (W_2) dissolved in a given volume of solvent of mass (W_1) at equilibrium pressure is given as

$$W_2 = KP \qquad ...(i)$$

Divide Eq. (i) by W_1 , the mass of solvent, we have

$$\frac{W_2}{W_1} = \frac{K}{W_1}P = K'P \quad \left(\frac{K}{W_1} = K'\right) \qquad \dots (ii)$$

Divide the two masses by their respective molar masses, we have

$$\frac{W_2/Mw_2}{W_1/Mw_1} = \left(\frac{K'Mw_1}{Mw_2}\right)P = K''P$$

$$m_2 \qquad \text{for each } (n) = \frac{W}{M}$$

or
$$\frac{n_2}{n_1} = K''P \quad \left(\text{moles } (n) = \frac{W}{Mw} \right)$$

The amount fraction of the gas in the solution is given as

$$\chi_2 = \frac{n_2}{n_1 + n_2} \qquad \qquad \dots (v)$$

If the solution is very dilute, i.e., $n_2 << 1$, Eq. (v) can be w_{ritte} as

$$\chi_2 = \frac{n_2}{n_1} \qquad \qquad \dots (v_i)$$

Now substituting this equation in Eq. (iv), we get

$$\chi_2 = K''P$$
or
$$P = \frac{1}{K''} \chi_2$$

$$P = K_H \chi_2 \qquad \left(K_H = \frac{1}{K''}\right) \qquad ...(vii)$$

where $K_{\rm H}$ is called Henry's law constant. Thus, Henry's law can also be stated as: the pressure of a gas over a solution in which the gas is dissolved is equal to the amount fraction of the dissolved gas multiplied by Henry's constant.

Different gases have different $K_{\rm H}$ values at the same temperature. This suggests that $K_{\rm H}$ is a function of the nature of the gas.

It is obvious from Eq. (vii) that the higher the value of $K_{\rm H}$ at a given pressure, the lower is the solubility of the gas in the liquid. $K_{\rm H}$ value for both N_2 and 0_2 increases with increase of temperature indicating that the solubility of gases decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

ILLUSTRATION 2.1

If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 L of water. Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

The solubility of gas is related to its mole fraction in the aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus,

$$\chi_{\text{N}_2} = \frac{p_{\text{N}_2}}{K_{\text{H}}} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

As 1 L water contains 55.5 mol of it, therefore, if n represents number of moles of N_2 in solution, then

$$\chi_{\text{N}_2} = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

Thus,
$$n = 1.29 \times 10^{-5} \times 55.5 \text{ mol}$$

= $7.16 \times 10^{-4} \text{ mol}$
= $7.16 \times 10^{-4} \text{ mol} \times \frac{1000 \text{ mmol}}{1 \text{ mol}}$
= 0.716 mmol

ILLUSTRATION 2.2

Henry's law constant for oxygen dissolved in water is 4.34×10^4 atm at 25°C. If the partial pressure of oxygen in air is 0.4 atm. Calculate the concentration (in moles per litre) of the dissolved oxygen in water in equilibrium with air at 25°C.

Sol.

··(Ŋ)

Given:

Henry's law constant,
$$K_{\rm H} = 4.34 \times 10^4$$
 atm

$$p_{\rm O_2} = 0.4 \text{ atm}$$

$$p = K_{\rm H} \chi$$

$$p_{O_2} = K_H \chi_{O_2}$$

or
$$\chi_{O_2} = \frac{p_{O_2}}{K_H} = \frac{0.4}{4.34 \times 10^4} = 9.2 \times 10^{-6}$$

Moles of water
$$(n_{\text{H}_2\text{O}}) = \frac{1000}{18} = 55.5 \text{ mol}$$

Mole fraction of oxygen
$$(\chi_{O_2}) = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}}$$

Since n_{O_2} is very small in comparison to n_{H_2O} ,

$$\therefore \chi_{O_2} = \frac{n_{O_2}}{n_{H_2O}}$$

or
$$\chi_{\text{O}_2} \times n_{\text{H}_2\text{O}} = n_{\text{O}_2}$$

$$9.2 \times 10^{-6} \times 55.5 = n_{O_2}$$

or
$$n_{O_2} = 5.11 \times 10^{-4} \,\text{mol}$$

Since 5.11×10^{-4} mol are present in 1000 mL of solution, therefore, molarity = 5.11×10^{-4} M.

ILLUSTRATION 2.3

Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.6. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is

a.
$$3.0 \times 10^{-4}$$

b.
$$4.0 \times 10^{-5}$$

c.
$$5.0 \times 10^{-4}$$

d.
$$6.0 \times 10^{-6}$$

Sol

a. Partial pressure of N₂ in air $(p_{N_2}) = P_{\text{total}} \times \chi_{N_2}(\text{in air})$

$$p_{N_2}$$
 (in air) = $K_H \times \chi_{N_2(\text{in H}_2O)}$

$$5 \times 0.6 = 1.0 \times 10^5 \times \chi_{\text{N}_2(\text{in H}_2\text{O})}$$

$$\chi_{N_2}$$
 in 10 moles of water = $\frac{5 \times 0.6}{1.0 \times 10^5} = 3.0 \times 10^{-5}$

$$\chi_{\rm N_2} = \frac{n_{\rm N_2}}{n_{\rm N_2} + n_{\rm H_2O}}$$

$$3.0 \times 10^{-5} = \frac{n_{\text{N}_2}}{n_{\text{N}_2} + 10}$$

$$n_{\text{N}_2} \times 3 \times 10^{-5} + 3 \times 10^{-5} \times 10 = n_{\text{N}_2}$$

 $3 \times 10^{-4} = n_{\text{N}_2} (1 - 3 \times 10^{-5})$ [1 - 3 × 10⁻⁵ \approx 1]

$$\therefore n_{\rm N_2} = 3 \times 10^{-4}$$

ILLUSTRATION 2.4

At same temperature, oxygen is more soluble in water than hydrogen. Which of them will have a higher value of $K_{\rm H}$ and why?

Sol. Hydrogen will have higher value of $K_{\rm H}$ because if gas has higher solubility, its $K_{\rm H}$ value is lower.

ILLUSTRATION 2.5

For a solution of acetone in chloroform, Henry's law constant is 150 torr at a temperature of 300 K. (a) Calculate the vapour pressure of acetone when the mole fraction is 0.12. (b) Assuming that Henry's law is applicable over sufficient range of composition to make the calculation valid, calculate the composition at which Henry's law pressure of chloroform is equal to Henry's law pressure of acetone at 300 K. (Henry's law constant for chloroform is 175 torr.)

Sol.

a. The given values are

$$K_{\rm H} = 150$$
 torr; $\chi_{\rm acetone} = 0.12$

Using Henry's law equation

 $P = K_{\rm H} \chi$, on substituting all values

$$P = (150 \text{ torr}) (0.12) = 18.0 \text{ torr}$$

b. Here P = 18.0 torr, and $K_{\rm H} = 175.0$ torr

$$\therefore \quad \chi_{\text{acetone}} = \frac{P}{K_{\text{H}}} = \frac{18.0 \text{ torr}}{175.0 \text{ torr}} = 0.103$$

ILLUSTRATION 2.6

Henry's law constant for oxygen and nitrogen dissolved in water at 298 K are 2.0×10^9 Pa and 5.0×10^9 Pa, respectively. A sample of water at a temperature just above 273 K was equilibrated with air (20% oxygen and 80% nitrogen) at 1 atm. The dissolved gas was separated from a sample of this water and then dried. Determine the composition of this gas.

Sol. The given values are:

$$K_{\text{H(O_2)}} = 2 \times 10^9 \text{ Pa}; \ K_{\text{H (N_2)}} = 5 \times 10^9 \text{ Pa}$$

Partial pressure of oxygen,

$$p_{\rm O_2} = 0.2 \text{ atm} = 20265 \text{ Pa}$$

Partial pressure of nitrogen;

$$[1 \text{ atm} = 101325 \text{ Pa}]$$

$$p_{\rm N_2} = 0.8 \text{ atm} = 81060 \text{ Pa}$$

Using Henry's law equation

$$\chi = \frac{P}{K_{\rm H}}$$

.. Mole fraction of O₂ in water

$$\chi_{\text{O}_2} = \frac{p_{\text{O}_2}}{K_{\text{H(O}_2)}} = \frac{20265}{2 \times 10^9} = 10.13 \times 10^{-6}$$

Mole fraction of N₂ in water

$$\chi_{N_2} = \frac{p_{N_2}}{K_{11(N_2)}} = \frac{81060}{5 \times 10^9} = 16.212 \times 10^{-6}$$

$$\therefore \frac{\text{Mole of dissolved oxygen}}{\text{Mole of dissolved nitrogen}} = \frac{10.13 \times 10^{-6}}{16.212 \times 10^{-6}} = 0.62$$

Hence, amount percent of
$$O_2 = \frac{0.62}{1.62} \times 100 = 38.27\%$$

Amount percent of
$$N_2 = 100 - 38.27 = 61.73\%$$

ILLUSTRATION 2.7

State Henry's law. What is the significance of K_H ?

Sol. Henry's law: It states that "the partial pressure of a gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution" and is expressed as

$$p = K_{\rm H} \chi$$

where $K_{\rm H}$ is Henry's law constant.

Significance of K_H : As $p_A = K_H \chi_A$. Thus, at constant temperature for the same partial pressure of different gases, $\chi_A \propto 1/K_H$. In other words solubility is inversely proportional to Henry's constant of the gas. Higher the value of K_H , lower is the solubility of the gas. As H_2 is more soluble than helium, H_2 will have lower value of K_H than that of helium.

APPLICATIONS OF HENRY'S LAW

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- **a.** To increase the solubility of CO₂ in soft drinks and soda water, the bottle is sealed under high pressure.
- b. To minimize the painful effects accompanying the decompression of deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.
- c. In lungs, where oxygen is present in air with high partial pressure, haemoglobin combines with oxygen to form oxy-haemoglobin. In tissues where the partial pressure of oxygen is low, oxohaemoglobin releases oxygen for utilization in cellular activities.
- d. Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends as well are the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- e. At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of climbers or people living at high altitudes. Low blood oxygen causes climbers to become weak and makes them unable to think clearly, symptoms of a condition known as anoxia.

LIMITATIONS OF HENRY'S LAW

Henry's law is valid only when

- a. Pressure is low.
- **b.** Temperature is low.
- c. The gas is not highly soluble.

d. The gas neither reacts chemically with the solvent hospitates or associates in the solvent.

Note: The effect of temperature on the solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. As dissolution is an exothermic process, the solubility should decrease with increase of temperature

2.5 SOLUBILITY OF A SOLID IN A LIQUID

The solubility of solids in liquids varies with the nature of solid and liquid, temperature, and to a lesser extent on the pressure of the system. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say like dissolves like.

When a solid solute is added to the solvent, some solute dissolves and concentration increases in solution. This process is called as *dissolution*. Some solute particle in solution collide with the solid solute particle and get separated out of solution. This process is known as *crystallization*. At equilibrium both dissolution and crystallization occur at the same rate at constant temperature and pressure. At this stage the concentration of solute in solution remains constant under the condition of constant temperature and pressure.

The solution at this stage in which no more solute can be dissolved at the same temperature and pressure is called saturated solution. An unsaturated solution is one in which more solute can be dissolved at same temperature and pressure. The maximum amount of solute that can be dissolved by the solvent at a particular temperature is called its solubility. Thus, the solubility of any substance at a given temperature is defined as the amount of the substance that dissolves in 100 g of the solvent at a given temperature to form a saturated solution.

Solubility of one substance into another depends on the nature of the substance. In addition to these, temperature and pressure also control this phenomenon. Temperature has a significant effect on the solubility of a solid substance into a solvent. The solubility may increases or decrease with increase in temperature. According to the Le Chatelier's principle, if the dissolution process is endothermic ($\Delta_{\text{sol}}H>0$), the solubility should increase with rise in temperature and if the process is exothermic the solubility should decrease, e.g., the solubility of sodium chloride (NaCl), potassium chloride (KCl), potassium iodide (KI) increases with rise in temperature, while solubility of calcium carbonate (CaCO₃) and lithium sulphate (Li₂SO₄) decreases with rise in temperature.

However, for some substances the solubility increases upto a certain temperature and then decreases with further rise in temperature. For these substances solubility behaviour not regular. For example, the solubility of sodium sulphate (Na₂SO₄) increases upto 32.8°C and above it the solubility decreases. This temperature corresponding to the break in the solubility curve is know as *transition temperature*. At transition temperature there is an equilibrium between sodium decahydrate Na₂SO₄.10H₂O and

anhydrous sodium sulphate (Na₂SO₄). Above this temperature only anhydrous sodium sulphate exists while below this temperature hydrated form exists.

pressure does not have any marked effect on the solubility of pressure does not have any marked effect on the solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by change in pressure.

2.6 VAPOUR PRESSURE OF LIQUID SOLUTION

Vapour pressure of a volatile liquid: Let us consider a liquid placed in a beaker and is covered with a jar (Fig. 2.6). The volatile liquid evaporates and occupy the space available in jar with its vapour. In the jar above the liquid surface the vapour molecules are in random motion; they collide with each other and get condensed into liquid, and eventually an equilibrium would be established between vapour phase and liquid phase. Thus, both evaporation and condensation processes go on simultaneously. The pressure exerted by the vapour molecules on the surface of liquid in the jar at equilibrium is called vapour pressure. Thus, the pressure exerted by the vapour above the liquid surface at equilibrium at a given temperature is called vapour pressure.

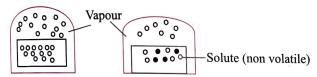


Fig. 2.6 (a) Pure solvent and (b) solvent and solute

The vapour pressure of liquid depends upon following parameters:

- Temperature: The vapour pressure of a liquid increases with increase in temperature. This is because on increasing the temperature the kinetic energy of molecules increases that results into the fact that more molecules escape from the surface of the liquid into the vapour phase resulting in higher vapour pressure.
- Nature of liquid: Every liquid has a different magnitude of intermolecular force. The liquids with weaker intermolecular forces tend to easily escape from liquid phase to vapour phase and hence they have higher vapour pressure, while those liquids which have strong intermolecular forces do not easily get vapourized so they have less vapour pressure.

Vapour pressure of solution containing volatile solvent in nonvolatile solute: In such solution only solvent molecules get vapourized and vapour pressure is solely from the solvent alone. This vapour pressure of the solution is found to be lower than the vapour pressure of pure solvent.

In the solution, the surface has both solute and solvent molecules, thereby a fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus the vapour pressure is also reduced. The decrease in the vapour pressure of solvent is directly proportional to the quantity of solute present in the solution irrespective of its

nature. For example, decrease in the vapour pressure of water by adding 1.0 mole of sucrose to 1 kg of water is nearly same to that produced by adding 1.0 mole of urea to the same quantity of water at the same temperature.

2.7 RAOULT'S LAW

The French chemist Francois Marie Raoult in 1886 observed that the partial vapour pressure of a solvent over a solution of a nonvolatile solute, p_{solution} is directly proportional to the mole fraction of the solvent in the solution (Fig. 2.7)

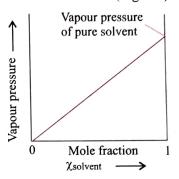


Fig. 2.7 If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent

Mathematically, such a relationship is described as

$$p_{\text{solution}} = \chi_{\text{solvent}} p_{\text{solvent}}^{\circ}$$
 ...(i)

where $p^{\circ}_{\text{solvent}}$ is the vapour pressure of the pure solvent at the given temperature. This relationship is known as Raoult's law, and the rearrangement of Eq. (i) gives

$$\frac{p_{\text{solution}}}{p_{\text{solvent}}^{\circ}} = \chi_{\text{solvent}} \qquad \dots (ii)$$

Thus, Raoult's law may be defined as: at a given temperature, the vapour pressure of a solution containing nonvolatile solute is directly proportional to the mole fraction of the solvent.

2.7.1 RAOULT'S LAW AS A SPECIAL CASE OF HENRY'S LAW

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $P_A = P^{\circ}_A \chi_A$. In the solution of a gas in a liquid, the gaseous component is so volatile that it exists as a gas and we have already seen that its solubility is governed by Henry's law that states that $P = K_H \chi$.

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Only the proportionality constant $K_{\rm H}$ differs from $P_{\rm A}{}^{\circ}$. Thus, Raoult's law becomes a special case of Henry's law in which $K_{\rm H}$ becomes equal to $P_{\rm A}{}^{\circ}$. Even in liquid solution, sometimes one of the components may obey Henry's law over a range of mole fraction. In practice, in the solution in which the solute behaves ideally according to Henry's law the solvent also behaves ideally according to Raoult's law (though the reverse is not necessarily true and Raoult's law ideality on the part of the solvent does not mean that the solute must obey Henry's law).

As a real solution approaches the limit of infinite dilution its components behave more ideal. The solvent obeys Raoult's law whereas solute (minor component) obeys Henry's law for dilute

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utions. This can be explained with the help of a systematic agram given below (Fig. 2.8).

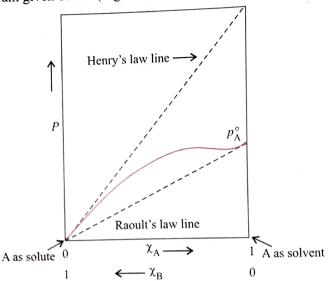


Fig. 2.8 Schematic graph indicating the applicability of Henry's law to the solute and Raoult's law to the solvent

In Fig. 2.8, we have a solution of liquids A and B. The partial ressure of A is plotted against its mole fraction in the solution, hence we get a curve as shown in Fig. 2.8. The curve according o Raoult's law can be obtained by connecting the zero point at the left $(\chi_A = 0)$ with the point representing p_A° at the right $\chi_A = 1$). It can be seen from Fig. 2.8 that Raoult's law curve meets the partial vapour pressure curve tangentially in the region where $\chi_A \to 1$. Thus, we see that Raoult's law is applicable only in the limited range of concentration where A is present in excess amount and is thus acting as a solvent. Now if we draw Henry's law curve and extraplot this line to the right axis, where $\chi_A = 1$, gives a hypothetical vapour pressure which would be observed only if Henry's law is applicable over the entire range of concentration, that is up to $\chi_A = 1$. Therefore, from Henry's law curve we observe that it meets to partial pressure curve only upto a small range at which A acts as solute ($\chi_A \approx 0$).

2.7.2 RAOULT'S LAW FOR A SOLUTION CONTAINING VOLATILE COMPONENTS

What happens when the solute and solvent both are volatile? Here, the vapour phase consists of vapours of both the components of the solution. The partial vapour pressure of each component of the solution depends on the mole fraction of the corresponding component. Let us consider a solution in which both the components obey Raoult's law marked as A and B with their mole fractions χ_A and χ_B , respectively. Their partial vapour pressures p_A and p_B are proportional to the respective mole fractions in the solutions.

Thus,
$$p_A \propto \chi_A$$

Similarly, $p_B \propto \chi_B$

Based on experimental findings, Raoult proposed that in case of mixture of two miscible liquids, the above relation written as follows holds good:

$$p_{\rm A} = p_{\rm A}^{\circ} \chi_{\rm A}$$
 ...(i)

$$p_{\rm B} = p_{\rm B}^{\circ} \chi_{\rm B}$$
 ...(ii)

where p_A° and p_B° represent the vapour pressures of pure components A and B, respectively. The relationship between

the vapour pressure of a component and its mole $fraction_{ig}$ another form of Raoult's law. This can be stated as: $for\ a\ sol_{ution}$ of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction. The law_{ig} applicable only when the two volatile liquids form a homogeneous solution.

A plot of p_A and p_B against χ_A or χ_B for a solution should give a straight line (Fig. 2.9).

These lines pass through points p_A° or p_B° when χ_A and χ_{θ} equals unity. According to Dalton's law of partial pressure, the total pressure of the solution for any composition is given as

$$p_{\text{total}} = p_{A} + p_{B} \qquad \dots (iii)$$

Here p_{total} is indicated in Fig. 2.9 by line III, obtained by joining the points p_{A}° and p_{B}° .

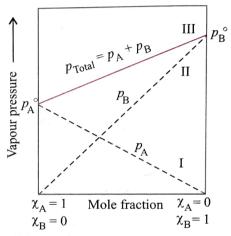


Fig. 2.9 The relationship between vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_{A} and p_{B} are directly proportional to χ_{A} and χ_{B} , respectively). The total vapour pressure is given by line III in the figure.

Solutions obeying Raoult's law are called *ideal liquid solutions*. Evidently for such solutions, the vapour pressure are intermediate between the values, $p_{\rm A}$ and $p_{\rm B}$ and they all lie on the straight lime joining $p_{\rm A}{}^{\circ}$ and $p_{\rm B}{}^{\circ}$.

Substituting the values of $p_{\rm A}$ and $p_{\rm B}$ in Eq. (iii), we get

$$p_{\text{total}} = \chi_{A} p_{A}^{\circ} + \chi_{B} p_{B}^{\circ} \qquad \dots (iv)$$

$$= (1 - \chi_{B}) p_{A}^{\circ} + \chi_{B} p_{B}^{\circ}$$

$$= p_{A}^{\circ} + (p_{B}^{\circ} - p_{A}^{\circ}) \chi_{B} \qquad \dots (v)$$

Following conclusions can be drawn from Eq. (v):

- a. Total vapour pressure over the solution can be related to the mole fraction of any one components.
- b. Total vapour pressure over the solution varies linearly with the mole fraction of component B.
- c. Depending on the vapour pressures of the pure components A and B, the total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component A.

The plot [line III (Fig. 2.9)] of p_{total} has minimum value of p_{A}° and maximum value is p_{B}° , assuming that component A is less volatile than component B, i.e., $p_{\text{A}}^{\circ} < p_{\text{B}}^{\circ}$.

[The composition of vapour phase can be determined with the help of Dalton's law of partial pressure.]

Let χ_A^V and χ_B^V are mole fractions of components A and B, respectively, in the vapour phase. Using Dalton's law of partial resure.

pressure
$$p_{A} = \chi_{A}^{V} p_{total}$$
and $p_{B} = \chi_{B}^{V} p_{total}$
or $\chi_{A}^{V} = \frac{p_{A}}{p_{total}} = \frac{\chi_{A} p_{A}^{\circ}}{p_{B}^{\circ} + (p_{A}^{\circ} - p_{B}^{\circ}) \chi_{A}}$

$$\chi_{B}^{V} = 1 - \chi_{A}^{V} = \frac{\chi_{B} p_{B}^{\circ}}{p_{A}^{\circ} + (p_{B}^{\circ} - p_{A}^{\circ}) \chi_{B}}$$

2.8 IDEAL AND NON-IDEAL SOLUTIONS

Binary solutions are classified into two categories: ideal solutions and non-ideal solutions.

1. Ideal solution:

A solution which obeys Raoult's law exactly at all range of concentration and temperature is known as ideal solution. In such solution the two components are identical in molecular size, shape, and have almost identical intermolecular forces. In these solutions, the intermolecular interaction between the unlike molecules (A–B) are of same magnitude as the intermolecular interaction between the like molecules, i.e., (A–A) and (B–B).

Then according to Raoult's law the partial pressure of two components of the solution is given as: $p_{\rm A} = \chi_{\rm A} p_{\rm A}^{\,\circ}$ and $p_{\rm B} = \chi_{\rm B} p_{\rm B}^{\,\circ}$. According to Dalton's law of partial pressure, the total pressure is given as $p_{\rm t} = p_{\rm A} + p_{\rm B}$ or $p_{\rm t} = \chi_{\rm A} p_{\rm A}^{\,\circ} + \chi_{\rm B} p_{\rm B}^{\,\circ}$.

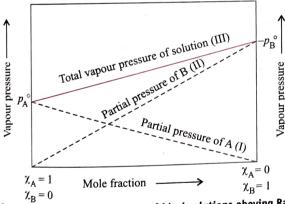


Fig. 2.10 Vapour pressure behaviour of ideal solutions obeying Raoult's law. The dashed lines I and II represent the partial vapour pressure of the components. The total vapour pressure is given by line III (solid line)

The total pressure $p_{\rm t}$ is shown by line III in Fig. 2.10 obtained by joining the points $p_{\rm A}^{\circ}$ and $p_{\rm B}^{\circ}$. It is clear from the figure that the vapour pressure of the solutions of different compositions, in case of ideal solutions, lies between the vapour pressure of the pure components $(p_{\rm A}^{\circ})$ and $(p_{\rm B}^{\circ})$.

Ideal solutions have two important properties:

- (a) Enthalpy of mixing $(\Delta_{mix}H)$: The enthalpy of mixing of pure components to form the solution is zero. It means that no heat is absorbed or evolved when the components are mixed, i.e., $(\Delta_{mix}H=0)$ because there is no change in magnitude of the attractive forces in the two components present.
- (b) Volume of mixing $(\Delta_{mix}V)$: In ideal solution, the change in volume on mixing is zero, i.e., $\Delta_{mix}V=0$. In such solution the volume of the solution is the sum of the volume of the components before mixing.

A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Examples of ideal solution are: (i) solution of n-hexane and n-heptane, (ii) benzene and toluene, (iii) ethyl bromide and ethyl chloride, (iv) chlorobenzene and bromobenzene, (v) benzene and xylene, (vi) ethylene dichloride (ClCH₂CH₂Cl) and ethylene dibromide (BrCH₂CH₂Br), (vii) CH₃OH + C₂H₅OH, and (viii) SnCl₄ + CCl₄.

2. Non-ideal solution:

A solution which does not obey Raoult's law is known as non-ideal solution.

$$p_{\rm A} \neq \chi_{\rm A} p_{\rm A}^{\ \circ}$$
 and $p_{\rm B} \neq \chi_{\rm B} p_{\rm B}^{\ \circ}$

In case of a non-ideal solution, the change in enthalpy of mixing $(\Delta_{\text{mix}}H)$ and change in volume on mixing $(\Delta_{\text{mix}}V)$ is not zero. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult's law. The cause for these deviations lies in the nature of interaction at the molecular level.

3. Types of non-ideal solutions:

(a) Non-ideal solutions showing positive deviation from Raoult's law: If in a binary solution of two components A and B, the interaction between the unlike components A–B are weaker than the interaction between the like components A–A and B–B, this means that in such solutions molecules of A (or B) will find it easier to escape than in pure state. This will result in having greater vapour pressure of each component of the solution than expected on the basic of Raoult's law, and hence the total vapour pressure will also be higher than in the case of ideal solution. This type of behaviour of solution is defined as positive deviation from Raoult's law.

In Fig. 2.11(a), a solution is exhibiting positive deviation. In such solution $p_{\rm A} > p_{\rm A}^{\circ} \chi_{\rm A}$ and $p_{\rm B} > p_{\rm B}^{\circ} \chi_{\rm B}$ and $p_{\rm total} > \chi_{\rm A} p_{\rm A}^{\circ} + \chi_{\rm B} p_{\rm B}^{\circ}$.

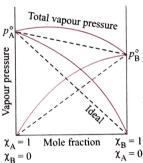


Fig. 2.11(a) Positive deviation from ideal behaviour. Dotted line represents ideal solution and dark line for non-ideal solution

A solution of ethanol and acetone behave in this way. In pure ethanol, molecules are held together with hydrogen bond as shown below.

$$C_2H_5 - O \cdots H - O \cdots$$

On adding acetone, the molecules of acetone get in between the host molecules breaking the hydrogen bonds of host molecules, this causes to weaken the intermolecular attraction between the alcohol molecules. This results into an increase in the escaping tendency of alcohol and acetone molecules from the solution. Consequently, the vapour pressure of the solution is greater than the vapour pressure expected from Raoult's law.

In such solution $\Delta_{mix}H$ is positive because energy is required to break A-A and B-B bonds. For such solutions, the dissolution process is endothermic, i.e., the solubility will increase with increase in temperature. $\Delta_{\rm mix} V$ is also positive for such solution because there is decrease in the magnitude of intermolecular forces in the solution, the molecules are loosely held, and therefore the volume of mixing increases.

Few examples of solution that shows positive deviation are:

- a. Ethyl alcohol and cyclohexane
- b. Acetone and carbon disulphide
- c. Benzene and acetone
- d. Carbon tetrachloride and chloroform
- e. Ethyl alcohol and water
- f. Acetone and ether

(b) Non-ideal solution showing negative deviation from Raoult's law: In such solution the interaction between the unlike molecules A-B is stronger than the interaction between the like ones, i.e., A-A and B-B. In the solution, molecules of A and B are strongly held due to stronger A-B interaction and therefore the escaping tendency of molecules of A or B becomes less than that of pure liquid. Consequently, each component has lesser partial pressure than that expected from Raoult's law. As a result, the total vapour pressure is less than that of ideal solution. These type of solutions are said to have negative deviation from Raoult's law.

Figure 2.11(b) shows a solution exhibiting negative deviation. In such solution $p_{\rm A} < \chi_{\rm A} p_{\rm A}{}^{\circ}$ and $p_{\rm B} < \chi_{\rm B} p_{\rm B}{}^{\circ}$ and $p_{\text{total}} < \chi_{A} p_{A}^{\circ} + \chi_{B} p_{B}^{\circ}.$

For example, a solution of chloroform and acetone shows negative deviation from Raoult's law. This is because in the solution the chloroform molecule is able to form hydrogen bond with the acetone molecule as shown below.

4. Mole fraction of solvent (A) in vapour phase = $\chi_A^V = \frac{p_A}{P_{\text{Total}}}$

Table 2.2 Comparison between ideal and non-ideal solutions

	Ton-ideal solutions	
Ideal solutions	Non-ideal solutions	
 Obey Raoult's law at every range of concentration. 	Positive deviation from Raoult's law a. Do not obey Raoult's law.	Negative deviation from Raoult's law
b. $\Delta_{\text{mix}}V = 0$; total volume of solution is equal to the sum of volumes of the	b. $\Delta_{\text{mix}} V > 0$. Volume is increased after dissolution	a. Do not obey Raoult's law.
components.	dissolution.	b. $\Delta_{\text{mix}} V < 0$. Volume is decreased during dissolution.
c. $\Delta_{mix}H = 0$; neither heat is evolved nor absorbed during dissolution.	c. $\Delta_{\text{mix}}H > 0$. Endothermic dissolution; heat is absorbed.	
d. A-A, A-B, B-B interactions should be same, i.e., A and B are identical in	d. A-B attractive force should	c. $\Delta_{\text{mix}}H < 0$. Exothermic dissolution; heat is evolved.
snape, size, and character.	than A-A and B-B attractive forces. A and B have different shape, size	d. A-B attractive force should be greater than A-A and B-B attractive forces A
e. $p = p_A + p_B = p_A^{\circ} \chi_A + p_B^{\circ} \chi_B$ i.e., $p_A = p_A^{\circ} \chi_A; p_B = p_B^{\circ} \chi_B$	e. $p_A > p_A^{\circ} \chi_A; p_B > p_D^{\circ} \gamma$	character.
	$\therefore p_{A} + p_{B} > p_{A}^{\circ} \chi_{A} + p_{B}^{\circ} \chi_{B}$	e. $p_A < p_A^{\circ} \chi_A; p_B < p_B^{\circ} \chi_B$ $p_A + p_A < p_A^{\circ} \chi_B$
A.		$\therefore p_{A} + p_{B} < p_{A}^{\circ} \chi_{A} + p_{B}^{\circ} \chi_{B}$

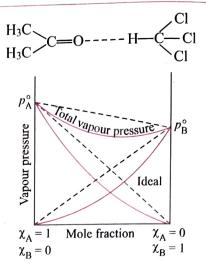


Fig. 2.11(b) Negative deviation from ideal behaviour. Dotted line represents ideal solution and dark line represents non-ideal solution

This newly formed hydrogen bond in the solution between the molecules of acetone and chloroform is stronger and decreases the escaping tendency of the liquid molecules from the solution Consequently the vapour pressure decreases resulting in negative deviation from Raoult's law. In this type of solution, $\Delta_{mix}H_{18}$ negative because on the formation of new attractive forces energy is released. Therefore, the dissolution process is exothermic and on heating the solubility of solution will decrease.

 $\Delta_{\text{mix}}V$ is also negative in such solution because on the formation of new attractive forces molecules comes closer to each other and are held more strongly. That results in the decrease in the volume on mixing, i.e., $\Delta_{mix}V$ is negative.

Few more examples of solution that show negative deviation are: acetone and chloroform, acetone and aniline, H₂O and HNO, chloroform and nitric acid, chloroform and diethyl ether, H_2O and HCl, H_2O and H_2SO_4 , $(H_2O + HNO_3)$, CH_3OH and CH_3COOH . and CH₃COOCH₃ and CHCl₃.

In Table 2.2, difference between ideal and non-ideal solutions is illustrated

f. Escaping tendency of A and B should be same in pure liquids and in the	f. A and B escape easily showing higher vapour pressure than the expected value.	f. Escaping tendency of both components A and B is lowered showing lower vapour pressure than expected ideally.
Examples Dilute solutions Benzene + Toluene n-Hexane + n-Heptane Chlorobenzene + Bromobenzene Ethyl bromide + Ethyl iodide n-Butyl chloride + n-Butyl bromide	Examples Acetone + Ethanol Acetone + CS ₂ Water + Methanol Water + Ethanol CCl ₄ + Toluene CCl ₄ + CHCl ₃ Acetone + Benzene CCl ₄ + CH ₃ OH Cyclohexane + Ethanol	Examples Acetone + Aniline Acetone + Chloroform CH ₃ OH + CH ₃ COOH H ₂ O + CH ₃ COOH Chloroform + Diethyl ether H ₂ O + HCl, H ₂ O + H ₂ SO ₄ , H ₂ O + HNO ₃ Acetic acid + Pyridine Chloroform + Benzene CH ₃ COOH + CHCl ₃

Why does the use of pressure cooker reduce cooking time?

At higher pressure over the liquid due to weight of the pressure cooker lid, the liquid starts boiling at higher temperature. Therefore, cooking occurs faster.

ILLUSTRATION 2.9

Why is the vapour pressure of a liquid constant at a constant temperature?

Sol. Vapour pressure is the pressure of the vapour at equilibrium state when the rate of evaporation becomes equal to the rate of condensation. The equilibrium constant does not change at a particular temperature and therefore the vapour pressure remains constant.

ILLUSTRATION 2.10

Two liquids A and B are mixed and the resulting solution is found to be cooler. What do you conclude about the deviation from ideal behaviour?

Sol. The solution shows positive deviation from ideal behaviour.

ILLUSTRATION 2.11

The dissolution of ammonium chloride in water is an endothermic process. What is the effect of temperature on its solubility?

Sol. Since solubility of NH₄Cl in water is an endothermic process, its solubility increases with rise in temperature (Le Chatelier's principle).

ILLUSTRATION 2.12

Mixing of acetone with chloroform takes place with reduction in volume? What type of deviation from Raoult's law is shown in this case?

Sol. The solution has negative deviation from Raoult's law because decrease in volume indicates strong forces of interaction between the molecules in solution.

ILLUSTRATION 2.13

CCl₄ and water are immiscible whereas ethanol and water are miscible in all proportions. Correlate this behaviour with molecular structure of these compounds.

Sol CCl₄ is a non-polar covalent compound, whereas water is a polar compound. CCl₄ can neither form H-bonds with water molecules nor can it break H-bonds in water molecules. Therefore, it is insoluble in water.

Ethanol is a polar compound and can form H-bonds with water, which is a polar solvent. Therefore, it is miscible with water in all proportions.

ILLUSTRATION 2.14

Vapour pressure of pure A (p_A°) = 100 mm Hg

Vapour pressure of pure B (p_B°) = 150 mm Hg

2 mol of liquid A and 3 mol of liquid B are mixed to form an ideal solution. The vapour pressure of solution will be:

Sol. b.
$$\chi_A = \frac{2}{5}, \ \chi_B = \frac{3}{5};$$

Using Raoult's law equation,

$$P_{\text{total}} = p_{\text{A}}^{\circ} \chi_{\text{A}} + p_{\text{B}}^{\circ} \chi_{\text{B}}$$

= $100 \times \frac{2}{5} + 150 \times \frac{3}{5} = 40 + 90 = 130$

ILLUSTRATION 2.15

The vapour pressure of pure benzene at 88°C is 957 mm and that of toluene at the same temperature is 379.5 mm. The composition of benzene—toluene mixture boiling at 88°C will be

a.
$$\chi_{\text{benzene}} = 0.66$$
; $\chi_{\text{toluene}} = 0.34$

b.
$$\chi_{\text{benzene}} = 0.34$$
; $\chi_{\text{toluene}} = 0.66$

c.
$$\chi_{\text{benzene}} = \chi_{\text{toluene}} = 0.5$$

d.
$$\chi_{\text{benzene}} = 0.75$$
; $\chi_{\text{toluene}} = 0.25$

2.14 Physical Chemistry

Sol.

1.
$$p = p_{\text{benzene}}^{\circ} \chi_{\text{benzene}} + p_{\text{toluene}}^{\circ} \chi_{\text{toluene}}$$

$$760 = 957 \chi_{\text{benzene}} + 379.5(1 - \chi_{\text{benzene}})$$

$$\chi_{\text{benzene}} = 0.66$$
and $\chi_{\text{toluene}} = 1 - 0.66 = 0.34$

ILLUSTRATION 2.16

The vapour pressure of a certain pure liquid A at 298 K is 40 mbar. When a solution of B is prepared in A at the same temperature, the vapour pressure is found to be 32 mbar. The mole fraction of A in the solution is

Sol.

d.
$$p = p^{\circ} \chi_{A}$$

 $32 = 40 \times \chi_{A} \text{ or } \chi_{A} = 0.8$

ILLUSTRATION 2.17

100 mL of liquid A and 25 mL of liquid B are mixed to form a solution of volume 125 mL. Then the solution is

- a. Ideal
- b. Non-ideal with positive deviation
- c. Non-ideal with negative deviation
- d. Cannot be predicted

a. $\Delta_{mix}V=0$, hence the solution is ideal.

ILLUSTRATION 2.18

An aqueous solution containing 28% by mass of liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 30°C. Find the vapour pressure of the pure liquid A. (The vapour pressure of water at 30°C is 150 mm.)

Sol. For two miscible liquids,

$$P_{\text{total}} = \text{Mole fraction of A} \times p_{\text{A}}^{\circ}$$

+ Mole fraction of B
$$\times p_B^{\circ}$$

Number of moles of A =
$$\frac{28}{140}$$
 = 2

Liquid B is water. Its mass is (100 - 28), i.e., 72.

Number of moles of B =
$$\frac{72}{18}$$
 = 4.0

Total number of moles =
$$0.2 \pm 4.0 = 4.2$$

Given,
$$p_{\text{total}} = 160 \text{ mm}$$

$$p_{\rm B}^{\circ} = 150 \text{ mm}$$

So,
$$160 = \frac{0.2}{4.2} \times p_{\text{A}}^{\ \ c} + \frac{4.0}{4.2} \times 150$$

$$p_{\rm A}^{\circ} = \frac{17.15 \times 4.2}{0.2} = 360.15 \,\rm mm$$

Questions Based on Mole Fraction of Solvent in Vapour Phase (χ^{V}_{A})

ILLUSTRATION 2.19

The vapour pressures of ethanol and methanol are 44.0 mm and 88.0 mm Hg, respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.

Sol. Mol. mass of ethyl alcohol (
$$C_2H_5OH$$
) = 46
Number of moles of ethyl alcohol = $\frac{60}{46}$ = 1.304

Mol. mass of methyl alcohol (
$$CH_3OH$$
) = 32

Number of moles of methyl alcohol =
$$\frac{40}{32}$$
 = 1.25

Mole fraction of ethyl alcohol,
$$\chi_A = \frac{1.304}{1.304 + 1.25}$$

$$= 0.5107$$
 Mole fraction of methyl alcohol, $\chi_B = \frac{1.25}{1.304 + 1.25}$

Partial pressure of ethyl alcohol=
$$\chi_A p_A^{\circ} = 0.5107 \times 44.0$$

Partial pressure of ethyl alcohol=
$$\chi_B p_B^{\circ} = 0.4893 \times 88.0$$

= 43.05 mm Hz

Total vapour pressure of solution =
$$22.47 + 43.05$$

= $65.52 \text{ mm } \text{Hz}$

Mole fraction of methyl alcohol in the vapour

$$= \frac{\text{Partial pressure of CH}_3\text{OH}}{\text{Total vapour pressure}} = \frac{43.05}{65.52} = 0.65\%$$

ILLUSTRATION 2.20

Two liquids A and B form ideal solution. At 300 K, the vapour pressure of a solution containing 1 mol of A and 3 mol of B is 500 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine vapour pressures of A and B in their pure states.

Sol. Let the vapour pressure of pure A be = p_A° ; and the vapour pressure of pure B be = p_B° .

Total vapour pressure of solution (1 mol A + 3 mol B)= $\chi_A p_A^{\circ} + \chi_B p_B^{\circ} [\chi_A]$ is mole fraction of A and χ_B is mole fraction of B1

$$500 = \frac{1}{4} p_{\rm A}^{\circ} + \frac{3}{4} p_{\rm B}^{\circ}$$

or
$$2000 = p_{A}^{\circ} + 3p_{B}^{\circ}$$
 ...(i)

Total vapour pressure of solution (1 mol A + 4 mol B) $=\frac{1}{5}p_{\rm A}^{\circ}+\frac{4}{5}p_{\rm B}^{\circ}$

$$510 = \frac{1}{5} p_{\rm A} \circ + \frac{4}{5} p_{\rm B} \circ$$

Mole fraction of component A in vapour phase is χ_1 and that of component A in liquid mixture is χ_2 ; then $(p_A^{\circ} = \text{vapour pressure})$ of pure A; p_B° = vapour pressure of pure B), the total vapour pressure of liquid mixture is

a.
$$p_A \circ \frac{\chi_2}{\chi_1}$$
 b. $p_A \circ \frac{\chi_1}{\chi_2}$ c. $p_B \circ \frac{\chi_1}{\chi_2}$ d. $p_B \circ \frac{\chi_2}{\chi_1}$

a.
$$p_A = p_A^{\circ} \chi_2$$
, vapour pressure of A.
Mole fraction of A in vapour = $\frac{p_A}{p_{\text{total}}}$
 $\chi_1 = \frac{p_A^{\circ} \chi_2}{P}$
 $p_{\text{total}} = \frac{p_A^{\circ} \chi_2}{\gamma_1}$

ILLUSTRATION 2.22

Heptane and octane form an ideal solution. At 373 K, the vapour pressure of the two liquids are 105.0 kPa and 46.0 kPa, respectively. What will be the vapour pressure, of the mixture of 25 g of heptane and 35 g of octane?

Sol.
$$Mw$$
 of heptane, C_7H_{16} , $Mw_A = 100$
 Mw of octane, C_8H_{18} , $Mw_B = 114$
 $n_A = \frac{W_A}{Mw_A} = \frac{25}{100} = 0.25$; $n_B = \frac{35}{114} = 0.3$
 $\chi_A = \frac{0.25}{0.25 + 0.30}$; $\chi_B = \frac{0.3}{0.25 + 0.30}$;
 $= 0.45 = 0.55$
 $P = p_A^{\circ} \chi_A + p_B^{\circ} \chi_B$
 $= 105.0 \times 0.45 + 46.0 \times 0.55$
 $= 47.25 + 25.30$
 $= 72.55$ kPa

ILLUSTRATION 2,23

Two liquids A and B form an ideal solution such that $p_A^{\circ} = 700 \text{ mm}$ and $p_{\rm B}^{\circ} = 300$ mm. A small amount of solution is vapourized and the vapour condensed (at equilibrium). The condensate has equilibrium vapour pressure of 500 mm (at same temperature). Find the composition of the original solution.

Sol.
$$P_{t} = P_{A} + P_{B}$$

$$P_{t} = p_{A} \circ \chi_{A} + p_{B} \circ \chi_{B} = 700 \chi_{A} + 300 (1 - \chi_{A}) \qquad \dots (i)$$

$$= 300 + 400 \chi_{A}$$

$$\chi_{A}^{v} = \frac{p_{A}}{P_{t}} = \frac{700 \chi_{A}}{300 + 400 \chi_{A}} = \frac{7 \chi_{A}}{3 + 4 \chi_{A}}$$

$$\chi_{B}^{v} = \frac{p_{B}}{P_{t}} = \frac{300 \chi_{B}}{300 + 400 \chi_{A}} = \frac{300 (1 - \chi_{A})}{300 + 400 \chi_{A}} = \frac{3 - 3 \chi_{A}}{3 + 4 \chi_{A}}$$

Put value in Eq. (i)
$$500 = 700 \left(\frac{7\chi_A}{3 + 4\chi_A} \right) + 300 \left(\frac{3 - 3\chi_A}{3 + 4\chi_A} \right)$$
$$\therefore \ \chi_A = 0.3, \chi_B = 0.7$$

ILLUSTRATION 2.24

At 80°C, the vapour pressure of pure liquid A is 520 mm Hg and that of pure liquid B is $1000\,\text{mm}$ Hg. If a mixture of solution A and B boils at 80°C and 1 atm pressure, the amount of A in the mixture is (1 atm = 760 mm Hg)

Sol. **a.**
$$P_{M} = p_{A}^{\circ} \chi_{A} + p_{B}^{\circ} \chi_{B}$$

$$P_{M} = p_{A}^{\circ} \chi_{A} + p_{B}^{\circ} (1 - \chi_{A})$$

$$760 = 520 \chi_{A} + 1000 - 1000 \chi_{A}$$

$$\chi_{A} = \frac{240}{480} = 0.5$$
Therefore, mol % = 50

ILLUSTRATION 2.25

At 298 K, the vapour pressure of pure liquid n-butane is 1823 torr and vapour pressure of pure liquid n-pentane is 521 torr and form nearly an ideal solution.

- a. Find the total vapour pressure at 298 K of a liquid solution containing 10% n-butane and 90% n-pentane by weight.
- **b.** Find the mole fraction of *n*-butane in solution exerting a total vapour pressure of 760 torr.
- c. What is composition of vapours of two components (mole fraction in vapour state)?

Sol.
$$P_{n\text{-butane}}^{\circ} = 1823 \text{ torr}$$
; $P_{n\text{-pentane}}^{\circ} = 521 \text{ torr}$

a. Given 10% *n*-butane by weight = 10 g 90% *n*-pentane by weight = 90 g

$$\therefore \text{ moles of } n\text{-butane} = \frac{10}{58} \left(Mw \text{ of } n\text{-butane} = 58 \right)$$

$$\text{moles of } n\text{-pentane} = \frac{90}{72} \left(Mw \text{ of } n\text{-pentane} = 72 \right)$$

$$\therefore \ \chi_{n\text{-butane}} = \frac{10/58}{10/58 + 90/72} = 0.122$$

$$\chi_{n\text{-pentane}} = 1 - \chi_{n\text{-butane}} = 1 - 0.122 = 0.878$$

From Raoult's law,

$$P_{\rm t} = P_{\rm A}^{\circ} \chi_{\rm A} + P_{\rm B}^{\circ} \chi_{\rm A} = 0.122 \times 1823 + 0.878 \times 521$$

= 679.84 torr

b. Given
$$P_{\text{total}} = 760 \text{ torr}$$
; $P_{n\text{-butane}}^{\circ} = 1823 \text{ torr}$; $P_{n\text{-pentane}} = 521 \text{ torr}$

Let mole fraction of *n*-butane =
$$y$$

mole fraction *n*-pentane = $1 - y$

$$P_{t} = P_{A}^{\circ} \chi_{A} + P_{B}^{\circ} \chi_{B}$$
$$760 = y(1823) + (1 - y)521$$

$$y = 0.183$$

c. The mole fraction in vapour state:

$$\chi^{\text{V}}_{\text{n-butane}} = \frac{P_{\text{n-butane}}}{P_{\text{total}}} = \frac{P^{\circ}_{\text{n-butane}} \times \chi_{\text{n-butane}}}{P_{\text{total}}}$$

$$= \frac{0.122 \times 1823}{679.84} = 0.327$$

$$\chi^{\text{V}}_{\text{n-pentane}} = \frac{P^{\circ}_{\text{n-pentane}} \times \chi_{\text{n-pentane}}}{P_{\text{total}}}$$

$$= \frac{521 \times 0.278}{679.84} = 0.673$$

 χ^{v} is also called as vapour fraction.

ILLUSTRATION 2.26

The vapour pressure of pure water at 25° C is 23.00 torr. What is the vapour pressure of 100 g of water to which 100 g of $C_6H_{12}O_6$ (glucose) has been added?

Sol. Raoult's law: $P_{\text{solution}} = p_A = p_A^{\circ} \chi_A$

$$\Rightarrow P_{\text{solution}} = p_{\text{A}}^{\circ} \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{B}}} = p_{\text{A}}^{\circ} \frac{\frac{W_{\text{A}}}{Mw_{\text{A}}}}{\frac{W_{\text{A}}}{Mw_{\text{A}}} + \frac{W_{\text{B}}}{Mw_{\text{B}}}}$$

$$\Rightarrow = 23.00 \times \frac{\frac{100}{18}}{\frac{100}{18} + \frac{100}{180}}$$

$$[Mw_{\text{Glucose}} = 180 \text{ g mol}^{-1}; p_{\text{A}}^{\circ} = 23.0 \text{ torr}]$$

$$\Rightarrow P_{\text{solution}} = 21.294 \text{ torr}$$

ILLUSTRATION 2.27

4.375 g of a substance when dissolved in 36.0 g of water, lowered its vapour pressure by 0.5 mm at a given temperature. The vapour pressure of water at this temperature is 25.0 mm. Calculate the molecular weight of solute.

Sol. $\Delta P = 0.5$ mm, using the formula for lowering of vapour pressure:

$$\frac{\Delta P}{P_{A}^{\circ}} = \chi_{B} = \frac{n_{B}}{n_{A} + n_{B}} = \frac{W_{B}/Mw_{B}}{W_{A}/Mw_{A} + W_{B}/Mw_{B}}$$

$$\Rightarrow \frac{0.5}{25} = \frac{4.375/Mw_{B}}{36/18 + 4.375/Mw_{B}}$$

$$\Rightarrow Mw_{B} = 109.38 \text{ g mol}^{-1}$$

ILLUSTRATION 2.28

Assuming ideal behaviour, calculate the pressure of 1.0 molal solution of a non-volatile molecular solute in water at 50°C. The vapour pressure of water at 50° C is 0.222 atm.

Sol. $P_{\text{solution}} = P_A = P_A^o \chi_A$ (Raoult's law) By using the relation between molality and mole fraction, we have;

$$m = \frac{\chi_{\rm B}}{\chi_{\rm A}} \times \frac{1000}{Mw_{\rm A}} = \frac{1 - \chi_{\rm A}}{\chi_{\rm A}} \times \frac{1000}{Mw_{\rm A}}$$

$$\Rightarrow \chi_{A} = \frac{1000}{\text{m}Mw_{A} + 1000}$$

$$= \frac{1000}{1 \times 18 + 1000} = \frac{1000}{1018} = 0.982$$

$$\Rightarrow P_{\text{solution}} = P_{A}^{\circ} \chi_{A} = 0.222 \times 0.982 = 0.218 \text{ atm}$$

ILLUSTRATION 2.29

At a certain temperature, the vapour pressure of pure ether is 640 mm and that of pure acetone is 280 mm. Calculate the mole fraction of each component in the vapour state if the $m_{0|\ell}$ fraction of ether in the solution is 0.50.

Sol. In the given solution, both ether and acetone are volatile so from Raoult's law, we can have vapour pressure of solution (P_{total}) .

Note:
$$\chi_{A \text{ (Liquid phase)}} = \frac{p_{A}}{p_{A}}$$
, $\chi_{A \text{(Vapour phase)}} = \frac{p_{A}}{p_{A} + p_{B}}$

Let A is ether and B is acetone.

$$P_{\text{total}} = p_{\text{A}} + p_{\text{B}} = p_{\text{A}}^{\circ} \chi_{\text{A}} + p_{\text{B}}^{\circ} \chi_{\text{B}}$$

= 640 × 0.5 + 280 × 0.5 = 460.0 mm

Now mole fraction in vapour state is given as follows:

$$\chi_{\text{A (vapour)}} = \frac{p_{\text{A}}}{P_{\text{total}}} = \frac{p_{\text{A}}^{\circ} \chi_{\text{A}}}{P_{\text{total}}} = \frac{640 \times 0.5}{460.0} = 0.6956$$

$$\chi_{\text{B (vapour)}} = \frac{p_{\text{B}}}{P_{\text{total}}} = \frac{p_{\text{B}}^{\circ} \chi_{\text{B}}}{P_{\text{total}}} = \frac{280 \times 0.5}{460.0} = 0.304$$

ILLUSTRATION 2.30

The vapour pressure of methyl alcohol at 298 K is 0.158 but. The vapour pressure of this liquid in solution with liquid B is 0.095 bar. Calculate the mole fraction of methyl alcohol in the solution if the mixture obeys Raoult's law.

Sol. Given
$$P_{\text{methyl alcohol}}^{\circ} = 0.158 \text{ bar}$$

$$P_{\text{solution}} = 0.095 \text{ bar}$$

According to Raoult's law

$$P = \chi_1 P^{\circ}$$
 $(\chi_1 = \text{mole fraction of methyl alcohol})$
 $\therefore 0.095 = \chi_1 \times 0.158$

$$\chi_1$$
 (mole fraction of methyl alcohol) = $\frac{0.095}{0.158} = 0.601$

ILLUSTRATION 2.31

The vapour pressure of acetone at 298 K is 40 mm of Hg. Is mole fraction in a solution with alcohol is 0.80. What is vapour pressure in solution if the mixture obey Raoult's law!

Sol. The given values are

$$P_{\text{acetone}}^{\circ} = 40 \text{ mm of Hg}$$

$$\chi_{acetone} = 0.80$$

According to Raoult's law

$$P_{A} = P_{A}^{\circ} \chi_{A}$$

On substituting all values, we get

Vapour pressure of acetone in solution =
$$40 \times 0.80$$

= $32 \text{ mm} \text{ of Hg}$

100 g of water contains 1.0 g urea and 2.0 g sucrose at 298 K. The vapour pressure of water at 298 K is 0.3 atm. Calculate the vapour pressure of the solution. (Molecular weight of urea = 60; Molecular weight of sucrose = 342)

The given values are

$$W_{\rm H_2O} = 100 \,\mathrm{g}$$
 ; $Mw_{\rm H_2O} = 18 \,\mathrm{g \, mol^{-1}}$
 $W_{\rm urea} = 10 \,\mathrm{g}$; $Mw_{\rm urea} = 60 \,\mathrm{g \, mol^{-1}}$
 $W_{\rm sucrose} = 2 \,\mathrm{g}$; $Mw_{\rm sucrose} = 342 \,\mathrm{g \, mol^{-1}}$

$$p_{\rm H_2O}^{\circ} = 0.3 \text{ atm}$$

Amount fraction of solvent

$$= \frac{\text{Amount of solvent}}{\text{Amount of (solvent + solute)}}$$

$$= \frac{100/18}{(100/18 + 1/60 + 2/342)}$$

$$= \frac{5.556}{5.577} = 0.99$$

According to Raoult's law,

$$p_A = p_A^{\circ} \chi_A$$

 \therefore Vapour pressure of solution = $0.3 \times 0.99 = 0.29$ atm

ILLUSTRATION 2.33

Benzene and toluene form nearly ideal solution. At 298 K, the vapour pressure of pure benzene is 150 torr and of pure toluene is 50 torr. Calculate the vapour pressure of the solution, containing equal weights of two substances at this temperature?

Sol. Let the weights of benzene and toluene in the solution is = W g

Mole fraction of benzene,
$$\chi_b = \frac{\frac{W}{78}}{\frac{W}{78} + \frac{W}{92}} = 0.541$$

Mole fraction of toluene $\chi_t = 1 - 0.541 = 0.459$

According to Raoult's law $p_A = p_A^{\circ} \chi_A$

:. Partial pressure of benzene,
$$p_B = p_b^{\circ} \times \chi_b = 150 \times 0.541$$

= 81.15 torr

$$\therefore$$
 Partial pressure of toluene, $p_t = p_t^{\circ} \times \chi_t = 50 \times 0.459$
= 22.95 torr

Total vapour pressure of solution =
$$p_b + p_t$$

= 81.15 + 22.95
= 104.1 torr

ILLUSTRATION 2.34

At 20°C, the vapour pressure of pure liquid A is 22 mm Hg and that of pure liquid B is 75 mm Hg. What is the composition of the solution of these two components that has vapour pressure of 48.5 mm Hg at this temperature?

The given values are $p_A^{\circ} = 22 \text{ mm Hg}$; $p_B^{\circ} = 75 \text{ mm Hg}$; $P_{\text{total}} = 48.5 \text{ mm Hg}$ Let χ_A and χ_B are the mole fractions of liquids A and B, respectively, in solution, then

$$p_{A} = p_{A}^{\circ} \chi_{A} = 22 \chi_{A}$$

 $p_{B} = p_{B}^{\circ} \chi_{B} = p_{B}^{\circ} (1 - \chi_{A}) = 75 (1 - \chi_{A})$
 $P_{\text{total}} = p_{A} + p_{B} = 22\chi_{A} + 75(1 - \chi_{A}) = 48.5$
 $\therefore \chi_{A} = 0.5 \text{ and } \chi_{B} = 1 - \chi_{A} = 0.5$

ILLUSTRATION 2.35

An aqueous solution containing 28% by weight of a liquid A (molecular mass = 140) has a vapour pressure of 0.200 bar at 37° C. Calculate the vapour pressure of pure liquid (vapour pressure of water at 37° C = 0.100 bar).

Sol. The given values are:

$$W_{\text{liquid}} = 28 \text{ g}, Mw_l = 140$$
 $W_{\text{H}_2\text{O}} = 72 \text{ g}; Mw_{\text{H}_2\text{O}} = 18$
 $p_{\text{H}_2\text{O}}^{\circ} = 0.10 \text{ bar}; P_{\text{total}} = 0.2 \text{ bar}$
Mole fraction of liquid, $\chi_l = \frac{28}{140} = 0.048$

Mole fraction of water, $\chi_{H_2O} = 1 - 0.048 = 0.952$

According to Raoult's law

$$\begin{split} &P_{\text{total}} = p_l^{\circ} \chi_l + p^{\circ}_{\text{H}_2\text{O}} \ \chi_{\text{H}_2\text{O}} \\ &0.2 = p_l^{\circ} \times 0.048 + 0.1 \times 0.952 \\ &\text{or } p_l^{\circ} = \frac{0.2 - 0.1 \times 0.952}{0.048} = 2.18 \text{ bar} \end{split}$$

Therefore, the vapour pressure of pure liquid is 2.18 bar.

ILLUSTRATION 2.36

Two liquids A and B have vapour pressure of 0.600 bar and 0.2 bar, respectively. In an ideal solution of the two, calculate the mole fraction of A at which the two liquids have equal partial pressures.

Sol. Let the mole fraction of $A = \chi$

Mole fraction of $B = 1 - \chi$

Partial pressure of $A = 0.6\chi$

Partial pressure of B = $0.2(1 - \chi)$

or $0.6\chi = 0.2(1 - \chi)$

y = 0.25

Hence, the mole fraction of A = 0.25.

ILLUSTRATION 2.37

Two liquids A and B have vapour pressures in the ratio of p_A° ; $p_B^{\circ} = 1:2$ at a certain temperature. Suppose we have an ideal solution of A and B in the mole fraction ratio A: B = 1:2. What would be the mole fraction of A in the vapour in equilibrium with the solution at a given temperature?

Sol.

b.
$$p_A^{\circ} : p_B^{\circ} = 1 : 2$$

 $p_A = \chi_A \times p_A^{\circ} = A \times \chi_A$

$$p_{B} = \chi_{B} \times p_{B}^{\circ} = 2A \times 2\chi_{A}$$

$$P_{\text{total}} = A\chi_{A} + 4 A\chi_{A} = 5A\chi_{A}$$

$$\chi_{A(\text{vapour phase})} = \frac{P_{A}}{P_{\text{total}}} = \frac{A\chi_{A}}{5A\chi_{A}} = \frac{1}{5} = 0.2$$

A certain ideal solution of two liquids A and B has mole fraction of 0.3 and 0.5 for the vapour phase and liquid phase, respectively. What would be the mole fraction of B in the vapour phase, when the mole fraction of A in the liquid is 0.25?

Sol.
$$\chi_{A}(\text{vap}) = 0.3, \chi_{B}(\text{liq}) = 0.5, \chi_{A}(\text{liq}) = 0.5$$

$$p_{A} = \chi_{A}p_{A}^{\circ} = 0.5p_{A}^{\circ}; p_{B} = \chi_{B}p_{B}^{\circ} = 0.5p_{B}^{\circ}$$

$$p_{\text{total}} = p_{A} + p_{B} = 0.5p_{A}^{\circ} + 0.5p_{B}^{\circ} = 0.5 (p_{A}^{\circ} + p_{B}^{\circ})$$

$$\chi_{A}(\text{vap}) = \frac{p_{A}}{p_{\text{total}}}$$

$$0.3 = \frac{0.5 p_{A}^{\circ}}{0.5 (p_{A}^{\circ} + p_{B}^{\circ})} = 0.3 = \frac{p_{A}^{\circ}}{p_{A}^{\circ} + p_{B}^{\circ}}$$
On rewriting it,
$$\frac{1}{0.3} = \frac{p_{A}^{\circ} + p_{B}^{\circ}}{p_{A}^{\circ}} = 1 + \frac{p_{B}^{\circ}}{p_{A}^{\circ}}$$

$$\Rightarrow \frac{p_{B}^{\circ}}{p_{A}^{\circ}} = \frac{1}{0.3} - 1 = \frac{0.7}{0.3} = \frac{7}{3}$$

$$\therefore \frac{p_{A}^{\circ}}{p_{B}^{\circ}} = \frac{0.3}{0.7} = \frac{3}{7} \Rightarrow p_{A}^{\circ} = \frac{3}{7}p_{B}^{\circ}$$

$$\chi_{A}(\text{liq}) = 0.25, \chi_{B}(\text{liq}) = 0.75$$

$$p_{A} = 0.25p_{A}^{\circ} = 0.25 \times \frac{3}{7}p_{B}^{\circ}$$

$$p_{B} = 0.75p_{B}^{\circ}$$

$$\therefore P_{\text{total}} = p_{A} + p_{B} = 0.25 \times \frac{3}{7}p_{B}^{\circ} + 0.75 p_{B}^{\circ}$$

$$= 0.75 \times \frac{8}{7}p_{B}^{\circ}$$

$$\chi_{B}(\text{vap}) = \frac{p_{B}}{p_{\text{total}}} = \frac{0.75 p_{B}^{\circ}}{0.75 \times \frac{8}{7}p_{B}^{\circ}} = \frac{7}{8}$$

ILLUSTRATION 2.39

Solution of two volatile liquids x and y obey Raoult's law. At a certain temperature it is found that when the total pressure above a given solution is 400 mm of Hg, the mole fraction of x in the vapour is 0.45 and in the liquid is 0.65. What are the vapour pressures of two pure liquids at the given temperature?

Sol.
$$\chi_x$$
 in liquid = 0.65
 χ_y in liquid = 0.35
 $p_x = \chi_x p_x^{\circ}$
 $p_y = \chi_y p_y^{\circ}$ $p_y = 0.35 p_y^{\circ}$ $p_x = 0.65 p_x^{\circ}$
 $p_{\text{total}} = p_x + p_y = 400$
 $\chi_x^{\circ} = 0.45 = \frac{p_x}{P_{\text{total}}}$

$$0.45 = \frac{0.65 \times p_{x}^{\circ}}{400}$$

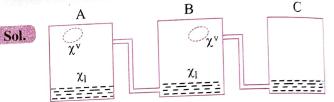
$$\therefore p_{x}^{\circ} = 276.9 \text{ mm}$$

$$0.65 \times 276.9 + 0.35p_{y}^{\circ} = 400$$

$$p_{y}^{\circ} = 628.6 \text{ mm}$$

ILLUSTRATION 2.40

Liquids X and Y form an ideal solution. The vapour pressure of X and Y at 100°C are 300 and 100 mm of Hg, respectively. Suppose that a solution composed of 1 mol of X and 1 mol of Y at 100°C is collected and condensed This condensate is then heated at 100°C and vapour is again condensed to form a liquid A. What is the mole fraction of X in A?



In vessel A

In vessel A
$$p_{X}^{\circ} = 300, p_{Y}^{\circ} = 100 \text{ mm}$$

$$\chi_{X} = \frac{1}{2}, \qquad \chi_{Y} = \frac{1}{2}$$

$$p_{X} = 300 \times \frac{1}{2} = 150,$$

$$p_{Y} = 100 \times \frac{1}{2} = 50$$

$$\chi_{X}^{\circ} = \frac{150}{200} = \frac{3}{4}$$

$$\chi_{Y}^{\circ} = 1 - \frac{3}{4} = \frac{1}{4}$$

In vessel B

$$\chi_{X}$$
 in B = $\frac{3}{4}$
 χ_{Y} in B = $\frac{1}{4}$
 $p_{X} = \chi_{X} \times p_{X}^{\circ}$
 $p_{X} = \frac{3}{4} \times 300 = 225$
 $p_{Y} = \chi_{Y} \times p_{Y}^{\circ}$
 $p_{Y} = \frac{1}{4} \times 100 = 25$
 $p_{X} + P_{Y} = 225 + 25 = 250$

$$\chi_X^{\text{v}} \text{ in B} = \frac{225}{250} = 0.9 \quad \begin{pmatrix} \because & \chi_X(\text{liquid}) = \chi_X^{\text{v}} \text{ in B} \\ & \text{in C Vessel} & \text{Vessel} \end{pmatrix}$$

A liquid mixture of benzene and toluene is composed of 1 mol of benzene and 1 mol of toluene.

- a. If the pressure over the mixture at 300 K is reduced, at what pressure does the first vapour form?
- b. What is the composition of the first trace of vapour formed?
- c. If the pressure is reduced further, at what pressure does the last trace of liquid disappear?
- d. What is the composition of the last trace of liquid?
- e. What will be the pressure, the composition of the liquid, and the composition of the vapour, when 1 mol of the mixture is vapourized?

Given:
$$p_T^{\circ} = 32.05 \text{ mm Hg}, p_B^{\circ} = 103 \text{ mm Hg}$$



a. The first vapour will be formed when the external pressure becomes equal to the vapour pressure of the system.

$$P = \chi_{\text{T}} p_{\text{T}}^{\circ} + p_{\text{B}}^{\circ} \chi_{\text{B}}$$

 $P = \frac{1}{2} (32.05) + \frac{1}{2} (103) = 67.52 \text{ mm Hg}$

b. Composition of the first trace of vapour formed

$$\chi_{\rm T} = \frac{P_{\rm T} \circ \chi_{\rm T}}{P} = \frac{0.5 \times 32.05}{67.52} = 0.24$$
$$\chi_{\rm R} = 1 - 0.24 = 0.76$$

c. The last trace of liquid will disappear when the composition of the vapour phase become $\chi_B=0.5$ and $\chi_T=0.5$. The pressure at which this occurs can be calculated as

$$\frac{1}{P} = \frac{\chi_{\rm T}}{P_{\rm T}^{\circ}} + \frac{\chi_{\rm B}}{P_{\rm B}^{\circ}} = \frac{0.5}{32.05} + \frac{0.5}{103}$$

$$P = 49.01 \text{ mm Hg}$$

d. Composition of the last trace of the liquid will be

$$\chi_{\rm B} = \frac{P_{\rm B}^{\circ} \chi_{\rm B}}{P}$$

$$0.5 = \frac{32.05 \chi_{\rm B}}{49.01}$$

$$\chi_{\rm B} = 0.76 \text{ and } \chi_{\rm T} = 0.24$$

e.
$$\chi_T = 0.642$$
, $\chi_B = 0.358$ and $\chi_B = 0.642$, $\chi_T = 0.358$, $P = 57.46$ mm Hg

ILLUSTRATION 2.42

Ethylene bromide C₂H₄Br₂, and 1,2-dibromopropane, C₃H₆Br₂, form a series of ideal solutions over the whole range of composition. At 85°C, the vapour pressure of these two pure liquids are 173 and 127 torr, respectively.

- a. If 10.0 g of ethylene bromide is dissolved in 80.0 g of 1,2-dibromopropane, calculate the partial pressure of each component and the total pressure of the solution at 85°C.
- b. Calculate the mole fraction of ethylene bromide in the vapour in equilibrium with the above solution.
- What would be the mole fraction of ethylene bromide in a solution at 85°C equilibrated with a 50:50 mole mixture in the vapour?

Sol.

a. Moles of $C_2H_4Br_2 = 10/188 = 0.0532$ Moles of $C_3H_6Br_2 = 80/202 = 0.396$ $\chi_{(C_2H_4Br_2)} = \frac{0.0532}{0.0532 + 0.396} = 0.118$ $P_{(C_2H_4Br_2)} = p^{\circ}\chi_{(C_2H_4Br_2)}$ $= 173 \text{ torr} \times 0.118 = 20.4 \text{ torr}$ $P_{(C_3H_6Br_2)} = p^{\circ}\chi_{(C_3H_6Br_2)} = 127 \text{ torr} \times 0.882 = 112 \text{ torr}$ $P_{\text{total}} = 20.4 + 112 = 132.4$

b.
$$\chi^{\text{v}}_{\text{(C}_2\text{H}_4\text{Br}_2)} = \frac{p_{\text{(C}_2\text{H}_4\text{Br}_2)}}{P_{\text{total}}} = 20.4/132.4 = 0.155$$

c.
$$P_{(C_2H_4Br_2)} = P_{(C_3H_6Br_2)}$$

 $173\chi_{(C_2H_4Br_2)} = 127\chi_{(C_3H_6Br_2)}$
 $= 127 (1 - \chi_{C_3H_4Br_2})$
 $173\chi = 127 (1 - \chi)$
 $300\chi = 127 \Rightarrow \chi = 0.423$.

ILLUSTRATION 2.43

The vapour pressures of two pure liquids A and B that form an ideal solution are 300 and 800 torr, respectively, at temperature T. A mixture of the vapours of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate

- a. The composition of the first drop of the condensate.
- b. The total pressure when this drop is formed.
- **c.** The composition of the solution whose normal boiling point is *T*.
- d. The pressure when only the last bubble of vapour remains.
- e. Composition of the last bubble.

Sol. Given

$$p_{A}^{\circ} = 300 \text{ torr},$$

 $\chi_{A}^{l} = 0.25, \chi_{B}^{l} = 1 - 0.25 = 0.75$

a. By the condensation of only one drop, we can assume that the composition of the vapour remains the same.

$$\chi_{A}^{V} = \frac{p_{A}^{\circ} \chi_{A}^{l}}{P_{T}} \text{ and } \chi_{B}^{V} = \frac{p_{B}^{\circ} \chi_{B}^{l}}{P_{T}}$$
or
$$\frac{\chi_{A}^{V}}{\chi_{B}^{V}} = \frac{p_{A}^{\circ} \chi_{A}}{p_{B}^{\circ} (1 - \chi_{A})}$$

Putting various known values, we get

$$\chi_{A}^{\ \ V} = 0.111$$
 and $\chi_{B}^{\ \ V} = 0.888$

- **b.** $p = p_A^{\circ} \chi_A^{V} + p_B^{\circ} \chi_B^{V}$ = $300 \times 0.11 + 800 \times 0.888$ = 743.7
- c. $760 = 300\chi_A + 800\chi_B$ $\chi_A = 0.08$ and $\chi_B = 0.92$
- **d.** When only the last bubble of vapour remains, we can assume the composition of vapour is now the composition of the condensate.

Hence,
$$P = 0.25 \times 300 + 0.75 \times 800 = 675$$
 torr

e. Composition of last bubble

$$\chi_{A} = \frac{p_{A} \circ \chi_{A}}{P} = \frac{0.25 \times 300}{675} = 0.11$$

$$\chi_{B} = 0.89$$

ILLUSTRATION 2.44

Calculate the vapour pressure lowering of a 0.1 m aqueous solution of non-electrolyte at 75°C.

$$\Delta H = 9.720 \text{ kcal mol}^{-1}, P_2 = 742.96 \text{ torr}$$

Sol. The vapour pressure of pure water, P_A° , at 75°C is

$$\log \frac{P_2}{P_1} = \frac{\Delta H^{\circ}}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$
$$= \frac{9720}{2.30 \times 1.978} \left(\frac{1}{348} - \frac{1}{373} \right) = 0.410$$

$$\frac{P_2}{P_1}$$
 = 2.51; P_1 = 296 torr

The vapour pressure lowering due to 0.100 m solute is

$$\Delta P = \frac{mMw_{\rm A}P_{\rm A}^{\circ}}{1000} = \frac{0.1 \times 18 \times 296}{1000} = 0.533$$

ILLUSTRATION 2.45

What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of (a) 0.400 and (b) 0.600?

$$p_{\rm b}^{\ \circ} = 119 \text{ torr}, p_{\rm t}^{\ \circ} = 37.0 \text{ torr}$$

Sol.
$$p_b = 0.400 \times 119 \text{ torr} = 47.6 \text{ torr}$$

 $p_t = 0.600 \times 37.0 \text{ torr} = 22.2 \text{ torr}$

$$p_{\text{total}} = (47.6 + 22.2) = 69.8 \text{ torr}$$

The composition of vapour is determined by applying Dalton's law of partial pressures:

$$\chi_{\rm b} = \frac{p_{\rm b}}{P_{\rm total}} = \frac{47.6}{69.8} = 0.682$$

$$\chi_{\rm b} = \frac{22.2}{69.8} = 0.318 = 1.000 - 0.682$$

Similarly, for the case of the solution in which the mole fraction of toluene is 0.400,

$$\chi_b = \frac{71.5}{86.3} = 0.829, \ \chi_t = \frac{14.8}{86.3} = 0.171$$

ILLUSTRATION 2.46

Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 600 torr, the amount fraction of A in the vapour phase is 0.40 and in the liquid phase is 0.60. What are the vapour pressures of pure A and pure B at temperature T?

Sol. The given data are

$$\chi_{A} = 0.60; \, \chi_{A}^{\ \ V} = 0.40; \, P_{t} = 600 \text{ torr}$$

$$p_{A}^{\circ} = ?, p_{B}^{\circ} = ?$$
Using equation $\chi_{i}^{\vee} = p_{i}/P_{\text{total}}$

$$\chi_{A}^{\vee} = \frac{p_{A}}{P} = \frac{\chi_{A}p_{A}^{\circ}}{P}$$
or $p_{A}^{\circ} = \frac{\chi_{A}^{\vee}p_{A}^{\circ}}{\chi_{A}} = \frac{(0.40)(600)}{(0.60)} = 400 \text{ torr}$
Similarly, $p_{B}^{\circ} = \frac{\chi_{B}^{\vee}P}{\chi_{B}} = \frac{(0.60)(600)}{(0.40)} = 900 \text{ torr}$

ILLUSTRATION 2.47

The vapour pressure of chloroform (CHCl₃) and dichloromethane (CH₂Cl₂) at 298 K is 200 mm Hg and 415 mm Hg, respectively. Calculate

- (a) The vapour pressure of the solution prepared by mixing 25.5 g of CHCl₃ and 40 g of CH₂Cl₂ at 298 K.
- (b) Mole fractions of each component in vapour phase.

Sol. (a) Molar mass of
$$CH_2Cl_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2$$

= 85 g mol⁻¹

Molar mass of CHCl₃ =
$$12 \times 1 + 1 \times 1 + 35.5 \times 3$$

= 119.5 g mol^{-1}

Moles of
$$CH_2Cl_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}$$

Moles of CHCl₃ =
$$\frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$$

Total number of moles = 0.47 + 0.213 = 0.683 mol

$$\chi_{CH_2Cl_2} = \frac{0.47 \; mol}{0.683 \; mol} = 0.688$$

$$\chi_{\text{CHCl}_3} = 1.00 - 0.688 = 0.312$$

$$P_{\text{total}} = p^{\circ}_{\text{CHCl}_3} + (p^{\circ}_{\text{CH}_2\text{Cl}_2} - p^{\circ}_{\text{CHCl}_3}) \chi_{\text{CH}_2\text{Cl}_2}$$

= 200 + (415 - 200) × 0.688
= 347.9 mm Hg

(b) To calculate the mole fraction of component in vapour phase,

$$\chi_i^{\text{V}} = \frac{p_i}{P_{\text{T}}}$$

$$p_{\text{CH}_2\text{Cl}_2} = 0.688 \times 415 \text{ mm Hg} = 285.5 \text{ mm Hg}$$

$$p_{\text{CHCl}_3} = 0.312 \times 200 \text{ mm Hg} = 62.4 \text{ mm Hg}$$

$$\chi_{\text{CH}_2\text{Cl}_2}^{} = \frac{285.5}{347.9} = 0.82$$

$$\chi_{\text{CHCl}_3}^{\ \ V} = \frac{62.4}{347.9} = 0.18$$

Note: Since CH_2Cl_2 is a more volatile component than $CHCl_3$ [p° $_{CH_2Cl_2}$ = 415 mm Hg and p° $_{CHCl_3}$ = 200 mm Hg] and the vapour phase is also richer in CH_2Cl_2 [$\chi^V_{CH_2Cl_2}$ = 0.82 and $\chi^V_{CH^{Cl_3}}$ = 0.18], it may be concluded that at equilibrium, vapour phase will be always rich in the component which is more volatile.

CONCEPT APPLICATION EXERCISE 2.1

- 1. At same temperature, the vapour pressure of pure benzene, is 0.20 bar and the vapour pressure of pure toluene is 0.09 bar. If the mole fraction of toluene in a solution is 0.60
 - What is the total vapour pressure of the solution?
 - Calculate the composition of the vapour in terms of mole fraction.
- 2. At 20°C, the vapour pressure of pure liquid A is 22 mm Hg and that of pure liquid B is 75 mm Hg. What is the composition of the solution of these two components that has a vapour pressure of 48.5 mm Hg at this temperature (assume ideal behaviour)?
- 3. Pressure of 0.210 bar at 37°C. Calculate the vapour pressure of pure liquid (vapour pressure of water at $37^{\circ}C = 0.198$ bar).

ANSWERS

1. a.
$$P_t = 0.134$$
 bar b. $\chi_{\text{benzene}}^{\text{V}} = 0.597$; $\chi_{\text{toluene}}^{\text{V}} = 0.402$

2.
$$\chi_A = 0.5 = \chi_B$$
 3. $P_l^{\circ} = 0.448$ bar

2.9 AZEOTROPIC MIXTURES

Binary mixtures that have same composition in liquid and vapour phase and boil at a constant temperature and can distil unchanged in composition are known as azeotropic mixtures or simply azeotropes (Greek meaning boiling without change). Thus, azeotropes behave as pure liquids.

There are two types of azeotropes called as minimum boiling azeotropes and maximum boiling azeotropes respectively.

(a) Minimum boiling azeotropes: The non-ideal binary solutions which show a very large positive deviation form Raoult's law form minimum boiling azeotropes at a constant composition. For example, the solution of ethanol-water shows a large positive deviation from Raoult's law (Fig. 2.12) as we can see from vapours-pressure-composition graph. A solution at a particular composition has a higher vapour pressure and a lower boiler point than for any one of its pure components. At this point the composition of liquid and vapour phases is same and the liquid boils at a constant temperature which is lower than the boiling temperature of either of the pure component (Fig. 2.13, temperature-composition graph).

We indicate the composition of the vapour phase by upper curve and composition of the liquid phase by lower curve. At the boiling point temperature ($T^{V} = 351$ K), the composition of an azeotrope its $\chi_{(H_2O)} = 0.056$ and $\chi_{(C_2H_5OH)} = 0.944$, while the boiling point of pure ethanol and water is 351.5 K and 373 K, respectively, which are higher than the boiling point of azeotrope. (Table 2.3)

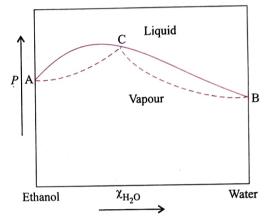


Fig. 2.12 Vapour pressure-composition graph

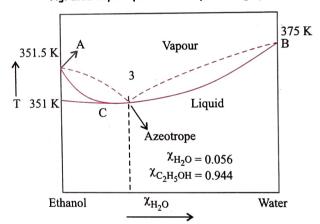


Fig. 2.13 Temperature-composition graph

Table 2.3 Some azeotropic mixtures

Components	Composition by	Boiling point			
A	В	weight % of B	A	В	Azeotrope
Minimum boiling	g azeotropes (positive	e deviations)			
H ₂ O	C ₂ H ₅ OH	95.57	373.00	351.5	351.15
H ₂ O	C ₃ H ₇ OH	71.69	373.00	370.19	350.72
(CH ₃) ₂ CO	CS ₂	67	329.25	319.25	312.25
CHCl ₃	C ₂ H ₅ OH	6.8	334.2	351.3	332.3
Maximum boilin	ng azeotropes (negati	ve deviations)			
H_2O	HCl	20,3	373.0	188	383
H ₂ O	HI	57.0	373.0	239	400
H ₂ O	HNO ₃	68.0	373.0	359	393.5
H ₂ O	HClO ₄	71.6	373.0	383	476
H ₂ O	H ₂ SO ₄	98.3%	373.0	-	611

The fractional distillation of solution will only give any one of the pure components (A or B) and azeotropic mixture c. The fractional distillation is able to concentrate the alcohol to its best, the azeotropic composition of approximately 95% by volume of ethanol. Once the composition has been obtained the liquid and vapour have the same composition and therefore, it cannot be further distilled to separate water, from ethanol. Other methods of separation have to be used for preparing 100% ethanol.

- (b) Maximum boiling azeotropes: The non-ideal solution which shows negative deviation from Raoult's law form maximum boiling azeotropes. From the vapour-pressure— composition diagram (Fig. 2.14), we can see that the solution has a minimum vapour pressure at a particular composition. This leads to a maximum on the boiling-point—composition diagram (Fig. 2.15). At this composition the solution boils at constant temperature without a change in the composition, i.e., the liquid phase and vapour phase have same composition. For example, a solution of HNO₃ and H₂O forms a maximum boiling point azeotropes. The composition of this azeotrope is 68% nitric acid and 32% water by mass and the boiling point is 393 K (Table 2.4).
- (c) Preparation of absolute alcohol: Absolute alcohol is prepared by azeotropic distillation method. Rectified spirit (95% C₂H₅OH) is mixed with a suitable amount of benzene and subjected to fractional distillation. The fractions obtained are shown in Table 2.4.

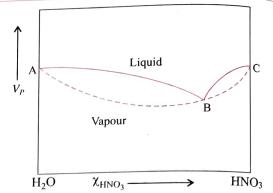


Fig. 2.14 Vapour pressure-composition diagram

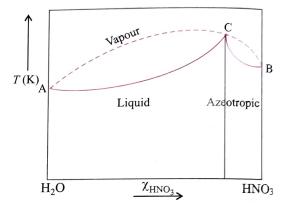


Fig. 2.15 Temperature-composition diagram

Table 2.4 Separation of azeotropes and preparation of absolute alcohol

Temperature	Azeotrope	Composition
331.8 K	Ternary azeotrope	H ₂ O : Benzene : Alcohol (7.4% : 74.1% : 18.5%)
341.2 K	Binary azeotrope	Benzene : Alcohol 67.7% : 32.2%
351 K	Absolute ethanol	

ILLUSTRATION 2.48

Why is an increase in temperature observed on mixing chloroform with acetone?

Sol. The bonds between chloroform molecules and molecules of acetone are dipole—dipole interactions, but on mixing, the chloroform and acetone molecules start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature.

ILLUSTRATION 2.49

The dissolution of ammonium chloride in water is an endothermic process but still it dissolves in water readily. Why?

Sol. This is because of entropy change. In this case, ΔS is positive.

$$NH_4Cl$$
 (aq) $\longrightarrow NH_4^{\oplus}$ (aq) + Cl^{\ominus} (aq)

The ions that were held together in the crystalline solid are free and move in all possible directions. Its entropy increases and then $T \Delta S > \Delta H$.

ILLUSTRATION 2.50

Two liquids X and Y boil at 110°C and 130°C, respectively. Which one of them has higher vapour pressure at 50°C?

Sol. Lower the boiling point, more volatile it is. Hence liquid X will have higher vapour pressure at 50°C.

ILLUSTRATION 2.51

Why does a solution of ethanol and cyclohexane show positive deviation from Raoult's law?

Sol. On adding cyclohexane, its molecules get in between the molecules of ethanol thus breaking the hydrogen bonds and reducing ethanol—ethanol interactions. This will increase the vapour pressure of the solution and result in positive deviation from Raoult's law.

ILLUSTRATION 2.52

What do you understand by colligative properties?

Colligative properties are those properties which depend the number of particles of solute but not on the nature of solute.

ILLUSTRATION 2.53

Name four important colligative properties of solutions of non-volatile solutes.

- Sol. a. Relative lowering of vapour pressure
 - b. Elevation in boiling point
 - c. Depression in freezing point
 - d. Osmotic pressure

ILLUSTRATION 2.54

Cutting onions taken from the fridge is more comfortable than cutting those lying at room temperature. Explain why.

At lower temperature, the vapour pressure is low. Less vapours of the tear-producing chemicals are produced.

ILLUSTRATION 2.55

Define an ideal solution.

Sol. An ideal solution is a solution which follows Raoult's law, $\Delta_{mix}H=0$, $\Delta_{mix}V=0$. In ideal solution the force of attraction between A-B is equal to that in A-A and B-B.

ILLUSTRATION 2.56

Two liquids A and B on mixing produce a warm solution. Which type of deviation from Raoult's law does it show?

Sol. Warming up of the solution means that the process of mixing is exothermic, i.e., $\Delta_{\text{mixing}}H$ is negative. This implies that the solution shows a negative deviation.

ILLUSTRATION 2.57

What type of liquids form ideal solutions?

Sol. Liquids that have similar structures and polarities form ideal solutions.

ILLUSTRATION 2.58

Under what condition do non-ideal solutions show negative deviations?

When the new forces of interaction between the components are greater than those in the pure components, non-ideal solutions show negative deviations.

ILLUSTRATION 2.59

What are constant boiling mixtures called?

Sol. Azeotropes.

ILLUSTRATION 2.60

What are maximum boiling azeotropes? Give one example.

Sol. Maximum boiling azeotropes are those which boil at higher temperature than boiling point of each component in pure state, e.g., H₂O and HCl.

ILLUSTRATION 2.61

What are minimum boiling azeotropes? Give one example.

Sol. Minimum boiling azeotropes are those which boil at lower temperature than boiling point of each component in pure state, e.g., H_2O and C_2H_5OH .

ILLUSTRATION 2.62

Give one example each of miscible liquid pairs showing positive and negative deviation from Raoult's law. Give one reason for each for such deviations.

Positive deviation from Raoult's law: A mixture of ethanol and cyclohexane shows positive deviation. When pure ethanol is added to cyclohexane the molecules of cyclohexane come in between the molecules of ethanol which results in the breaking of hydrogen bonds and thus positive deviation.

$$\cdots$$
 H $-$ O \cdots H $-$ O \cdots H $-$ O \cdots H $-$ O \cdots C₂H₅ C₂H₅ C₂H₅

Negative deviation from Raoult's law: A mixture of chloroform and acetone shows negative deviation. When these are mixed, hydrogen bond is formed and negative deviation is shown:

$$CI$$
 CI
 CH_3
 CH_3

ILLUSTRATION 2.63

Can we separate the components of azeotropic mixture by distillation?

Sol. No, we cannot separate the components of an azeotropic mixture by distillation because at a particular composition, both the components boil at the same temperature.

2.10 COLLIGATIVE PROPERTIES

In this section we have learnt that the vapour pressure of a solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (a) relative lowering of the vapour pressure of the solvent. (b) depression in the freezing point of the solvent; (c) elevation in the boiling point of the solvent, and (d) osmotic pressure of the solution.

All the properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called *colligative properties* (colligative, from latin: *co* means together, *ligare* means to bind).

2.10.1 RELATIVE LOWERING OF VAPOUR PRESSURE

Recall that the vapour pressure of a solvent in a solution is less than that of pure solvent, that is because in solution only solvent molecules contribute to the total vapour pressure since the solute is non-volatile. Then, according to Raoult's law, the total vapour pressure of solution is equal to the mole fraction of solute multiplied to the vapour pressure of pure solvent, i.e.,

$$P_{\text{solution}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ} \qquad \dots (i)$$

 $(P_{\text{solvent}}^{\circ} = \text{vapour pressure of pure solvent}, \chi_{\text{solvent}} = \text{mole fraction}$ of solvent, $P_{\text{solution}} = \text{vapour pressure of solution})$

The reduction in vapour pressure of solvent (ΔP_A) is given as

$$\Delta P_{\mathbf{A}} = P_{\mathbf{A}}^{\ \ c} - P_{\mathbf{A}} \qquad \dots (ii)$$

$$=P_{\mathbf{A}}^{\circ}-\chi_{\mathbf{A}}P_{\mathbf{A}}^{\circ} \qquad(iii)$$

$$=P_{\Delta}^{\circ}(1-\chi_{\Delta}) \qquad ...(iv)$$

Knowing that $\chi_B = 1 - \chi_A$, i.e., total mole fraction is one.

Then, Eq. (iv) reduces to

$$\Delta P_{\mathbf{A}} = P_{\mathbf{A}}^{\circ} \mathbf{\chi}_{\mathbf{B}} \qquad \dots (\mathbf{v})$$

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Equation (v) can be written as

$$\frac{\Delta P}{P_{A}^{\circ}} = \left(\frac{P_{A}^{\circ} - P_{S}}{P_{A}^{\circ}}\right) = \chi_{B} \qquad \dots (vi)$$

Equation (vi) is called the *relative lowering of vapour pressure* and is equal to the mole fraction of the solute.

Determination of Molar Mass of Solute from Relative Lowering of Vapour Pressure

The molecular mass of the solute can be determined by the relativing lowering of vapour pressure. Equation (vi) can be rewritten as

$$\therefore \frac{P_A^{\circ} - P_S}{P_A^{\circ}} = \chi_B = \frac{n_B}{n_B + n_A} \qquad \dots (vii)$$

(where n_B and n_A are mole numbers of solute, and solvent, respectively)

$$n_{\rm B} = \frac{W_{\rm B}}{Mw_{\rm B}} \ ; n_{\rm A} = \frac{W_{\rm A}}{Mw_{\rm A}}$$

 $(Mw_A; Mw_B = \text{molecular weight of solvent}$ and solute, respectively; W_A , $W_B = \text{weight}$ of solvent and solute, respectively)

$$\therefore \frac{P_A^{\circ} - P_S}{P_A^{\circ}} = \frac{\frac{W_B}{Mw_B}}{\frac{W_A}{Mw_A} + \frac{W_B}{Mw_B}} \qquad \dots (viii)$$

For a very dilute solution, $n_B \ll n_A$. Hence, n_B is negligible in comparison to n_A .

Then, Eq. (viii) reduces to

$$\frac{P_{A}^{\circ} - P_{S}}{P_{A}^{\circ}} = \frac{W_{B}}{Mw_{B}} / \frac{W_{A}}{Mw_{A}} \qquad ...(ix)$$
or
$$\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} = \frac{W_{\text{solute}} \times Mw_{\text{solvent}}}{Mw_{\text{solute}} \times W_{\text{solvent}}}$$

Thus, the molar mass of the solute can be determined if the other quantities, i.e., W_{solute} , W_{solvent} , Mw_{solvent} , and the relative

lowering of vapour pressure
$$\left[\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}}\right]$$
, are k_{nown}

ALTERNATE FORMULA FOR THE RELATIVE LOWERING OF VAPOUR PRESSURE WHEN THE SOLUTION IS NOT DILUTE

$$\frac{P_{\text{solvent}}^{\circ} - P_{\text{solution}}}{P_{\text{solvent}}^{\circ}} \text{ or } \frac{P^{\circ} - P_{\text{S}}}{P^{\circ}} = \frac{n_{\text{B}}}{n_{\text{A}} + n_{\text{B}}}$$

On reversing Eq. (i), we get

$$\frac{P^{\circ}}{P^{\circ} - P_{S}} = \frac{n_{A} + n_{B}}{n_{B}} = 1 + \frac{n_{A}}{n_{B}}$$

$$\Rightarrow \frac{P^{\circ}}{P^{\circ} - P_{S}} - 1 = \frac{n_{A}}{n_{B}}$$

$$\Rightarrow \frac{P^{\circ} - P^{\circ} + P_{S}}{P^{\circ} - P_{S}} = \frac{n_{A}}{n_{B}}$$

$$\Rightarrow \frac{P_{S}}{P^{\circ} - P_{S}} = \frac{n_{A}}{n_{B}}$$
or
$$\frac{P^{\circ} - P_{S}}{P_{S}} = \frac{n_{B}}{n_{A}}$$

Note: This equation can be used to solve the problem quickly, whether the solution is dilute or not.

Experimental Method for the Determination of Vapour Pressure Lowering

Static method

- a. Raoult's bassometric method
- b. Differential barrometric method

Dynamic method

- Ostwald and Walker method
- b. Differential barrometric method
- c. Transpiration method

Ostwald and Walker method: The relative lowering in vapour pressure is determined by Ostwald and Walker method. The experimental setup is shown in Fig. (2.16). It consists of two sets of bulbs. The first set of three bulbs is filled with solution. To half of their capacity and the second set of another three bulbs is filled with the pure solvent

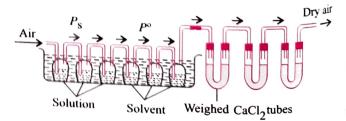


Fig. 2.16 Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents such as P₂O₅, concentrated H₂SO₄, etc.

2.25

A current of pure dry air is bubbled through the series of bulbs as $\frac{1}{1}$ A current of pure dry air is bubbled through the vapours in each $\frac{1}{1}$ set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapour from the solvent which is proportional to the difference in the vapour pressure of solvent and the vapour pressure of solution, i.e., $P^{\circ} - P_{S}$. The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto P_S$ Loss in mass in the solvent bulbs $\propto (P^\circ - P_S)$ Total loss in the both sets of bulbs $\propto [P_S + (P^\circ - P_S)]$ $\propto P^\circ$

Total loss in the mass of both sets of bulbs is equal to gain in the mass of guard tubes.

Thus,
$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$

$$= \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further we know from Raoult's law,

$$\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} = \frac{W_{\rm B}/Mw_{\rm B}}{W_{\rm A}/Mw_{\rm A} + W_{\rm B}/Mw_{\rm B}}$$

Hence.

$$\frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{W_{\text{B}}/Mw_{\text{B}}}{W_{\text{A}}/Mw_{\text{A}} + W_{\text{B}}/Mw_{\text{B}}}$$

The above relationship is used for the calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied:

$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{W_{B}/Mw_{B}}{W_{A}/Mw_{A}}$$

LLUSTRATION 2.64

Calculate the molal lowering of vapour pressure for H₂O at 100°C.

Sol.
$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \frac{n_{2}}{n_{2} + n_{1}}$$

$$P^{\circ} - P_{S} = P^{\circ} \left[\frac{n_{2}}{n_{2} + n_{1}} \right]$$

Let 1 mol of solute is dissolved in 1000 g solvent water.

Thus,
$$n_2 = 1$$
 and $n_1 = \frac{1000}{18}$

Also, $P^{\circ} = 760 \text{ mm}$ for water at 100° C.

$$P^{\circ} - P_{\rm S} = \left[\frac{1}{1 + \frac{1000}{18}} \right] \times 760 = 13.43 \text{ mm}$$

ILLUSTRATION 2.65

A current of dry air was bubbled through a bulb containing 26.66 g of an organic compound in 200 g of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in the bulb containing water was 0.087 g and the gain in the mass of the calcium chloride tube was 2.036 g. Calculate the molecular mass of the organic substance.

Sol.
$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \frac{\text{Loss in mass of solvent bulb}}{\text{Gain in mass of CaCl}_{2} \text{ tube}}$$
$$= \frac{0.087}{2.036}$$

Let the molecular mass of the organic substance be Mw_2 . According to Raoult's law,

$$\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} = \frac{W_2/Mw_2}{\frac{W_2}{Mw_2} + \frac{W_1}{Mw_1}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{Mw_2}}{\frac{26.66}{Mw_2} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18}Mw_2}$$

$$Mw_2 = 53.75$$

ILLUSTRATION 2.66

What mass of non-volatile solute (urea) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 30%. What will be the molality of solution?

Sol. Using Raoult's law in the following form,

$$\frac{P^{\circ} - P_{\rm S}}{P_{\rm S}} = \frac{W_2 M w_1}{W_1 M w_2}$$
If $P^{\circ} = 100$ mm, then $P_{\rm S} = 70$ mm
$$\frac{100 - 70}{70} = \frac{W_2 \times 18}{100 \times 60}$$

$$0.43 = \frac{W_2 \times 18}{100 \times 60} \Rightarrow W_2 = 143.33$$
Molality = $\frac{W_2 \times 1000}{M w_2 \times W_1} = \frac{143.33 \times 1000}{60 \times 100} = 23.88$

ILLUSTRATION 2.67

A solution containing 30 g of a non-volatile solute in exactly 90 g of water has a vapour pressure of 21.85 mm of Hg at 25°C. Further 18 g of water is then added to the solution; the new vapour pressure becomes 22.15 mm of Hg at 25°C. Calculate the (a) molecular mass of the solute and (b) vapour pressure of water at 25°C.

Sol. Let the vapour pressure of water at 25°C be P° and molecular mass of the solute be Mw_2 .

Using Raoult's law in the following form,

$$\frac{P^{\circ} - P_{S}}{P_{S}} = \frac{W_2 M w_1}{W_1 M w_2}$$

For solution (I),
$$\frac{(P^{\circ} - 21.85)}{21.85} = \frac{M}{2}$$
 ...(i)

For solution (II),
$$\frac{(P^{\circ} - 22.15)}{22.15} = \frac{30 \times 18}{108 \times Mw_2}$$
 ...(ii)

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{(P^{\circ} - 21.85)}{21.85} \times \frac{22.15}{(P^{\circ} - 22.15)} = \frac{108}{90} = \frac{6}{5}$$

$$P^{\circ} = 23.87 \text{ mm of Hg}$$

Substituting the value of P° in Eq. (i), we get

$$Mw_2 = 67.9$$

ILLUSTRATION 2.68

The vapour pressure of a dilute aqueous solution of glucose is 700 mm Hg at 370 K. Calculate the (a) molality and (b) mole fraction of the solute.

Sol. P° = Vapour pressure of water at 373 K = 760 mm Hg Using Raoult's law in the following form,

$$\frac{P^{\circ} - P_{\rm S}}{P_{\rm S}} = \frac{W_2 M w_1}{W_1 M w_2}$$

or
$$\frac{760 - 700}{700} = \frac{W_2 \times 18}{W_1 \times Mw_2}$$

or
$$\frac{W_2}{W_1 \times Mw_2} = \frac{60}{700 \times 18}$$

Molality =
$$\frac{W_2}{W_1 \times Mw_2} \times 1000 = \frac{60 \times 1000}{700 \times 18} = 4.76 \text{ m}$$

 P_{ς} = Mole fraction of solvent $\times P^{\circ}$;

Mole fraction of solvent =
$$\frac{700}{760}$$
 = 0.921

So, mole fraction of solute = 1 - 0.921 = 0.0789

ILLUSTRATION 2.69

10 g of glucose (molar mass 180) and 20 g of sucrose (molar mass 342) are dissolved in 100 g of water. What will be the vapour pressure of the resultant solution if the vapour pressure of water is 30 mm Hg?

Sol. Mass of glucose = 10 g

Number of moles of glucose = 0.0556

Mass of sucrose = 20 g

Number of moles of sucrose = 0.0585

Mass of water = 100 g

Number of moles of water = 5.556

Total number of moles = 5.556 + 0.0585 + 0.0556 = 5.67

Mole fraction of water = $\frac{5.556}{5.67}$

Vapour pressure of solution = Mole fraction of water $\times P^{\circ}$

$$= \frac{5.556}{5.67} \times 30 = 29.3 \text{ mm Hg}$$

ILLUSTRATION 2.70

Calculate the vapour pressure of an aqueous solution of 1.0 molal glucose solution at 100°C.

Sol. Molality =
$$\frac{W_2}{Mw_2 \times W_1} \times 1000$$

where W_2 = mass of solute in grams;

 $W_1 = \text{mass of solvent in grams}$

$$1.0 = \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

or
$$\left(\frac{K}{W_1} = K'\right) = \frac{1.0}{1000} = 0.001$$

Applying Raoult's law for dilute solution,

$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \frac{W_{2}}{Mw_{2} \times W_{1}} \times Mw_{1} \qquad [Mw_{1} = 18]$$

$$\frac{760 - P_{\rm S}}{760} = 0.001 \times 18 \qquad [P^{\circ} = 760 \text{ mm at } 100^{\circ}\text{C}]$$
or $P_{\rm S} = 760 - 760 \times 0.001 \times 18$

$$= 760 - 13.68$$

= 746.32 mm Hg

ILLUSTRATION 2.71

The vapour pressure of pure benzene at 50°C is 268 mm of Hg. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure of 160.0 mm of Hg at 50°C?

Sol. Applying Raoult's law in the following form:

$$\frac{P^{\circ} - P_{\rm S}}{P_{\rm S}} = \frac{W_2/Mw_2}{W_1/Mw_1}$$

= Number of moles of solute per mole of

benzene

or
$$\frac{n_2}{n_1} = \frac{(286 - 160)}{160} = 0.675$$

Alternative method

We know that P_S = Mole fraction of solvent \times P° or 160 = Mole fraction of solvent \times 268

So, molar fraction of solvent =
$$\frac{160}{268}$$
 = 0.597

Mole fraction of solute = 1 - 0.597 = 0.403

$$\frac{n_2}{n_1} = \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent}} = \frac{0.403}{0.597} = 0.675$$

ILLUSTRATION 2.72

Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is

- a. 13.44 mm Hg
- **b.** 14.12 mm Hg
- c. 13.2 mm Hg
- **d.** 35.2 mm Hg

Sol.
$$a.\ Mw_{\rm B} = \frac{\chi_{\rm B} \times 1000}{(1 - \chi_{\rm B})Mw_{\rm A}}$$

$$1 = \frac{\chi_{\rm B} \times 1000}{(1 - \chi_{\rm B}) \times 18}$$

$$\chi_{\rm B} = 0.0176$$

$$\chi_{\rm A} = 1 - 0.0176 = 0.9824$$

$$P = P^{\circ}\chi_{\rm A} = 760 \times 0.9824 = 746.62$$

$$\Delta P = P^{\circ} - P = 760 - 746.62 \approx 13.41$$

Calculate the vapour pressure lowering caused by the addition of 68.4 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 20.0 mm Hg.

Sol.

According to Raoult's law.

$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \frac{n_{2}}{n_{2} + n_{1}} = \chi_{2}$$
or $\Delta P = \frac{n_{2}}{n_{2} + n_{1}} P^{\circ}$
Given: $n_{2} = \frac{68.4}{342} = 0.20$: $n_{1} = \frac{500}{18} = 27.78$ and $P^{\circ} = 20.0$

Substituting the values in the above equation, we get

$$\Delta P = \frac{0.20}{0.20 + 27.78} \times 20.0 = 0.142 \text{ mm Hg}$$

ILLUSTRATION 2.74

Calculate the vapour pressure of an aqueous solution which contains 5 mass per per cent of urea. The vapour pressure of pure water is 23.5 mm Hg. The molar mass of urea is 60.

Mass of urea
$$= 5 g$$

Mass of water =
$$(100 - 5) = 95$$
 g

Number of moles of urea =
$$\frac{5}{60}$$
 = 0.083

Number of moles of water =
$$\frac{95}{18}$$
 = 5.278

Total number of moles =
$$5.278 + 0.083$$

= 5.301

Mole fraction of solvent =
$$\frac{5.278}{5.361}$$

$$P_{\rm S}$$
 = Mole fraction of solvent × P°
= $\frac{5.278}{5.361}$ × 23.5 = 23.14 mm Hg

ILLUSTRATION 2.75

The relative lowering of the vapour pressure of an aqueous solution containing a non-volatile solute is 0.0125. The molality of the solution is

b. 0.50

c. 0.70

d. 0.40

Sol. c. As we know

$$\frac{P^{\circ} - P}{P^{\circ}} = \chi_2 = \text{mole fraction of solute}$$

The ratio $(P^{\circ} - P)/P^{\circ}$ is the relative lowering of vapour pressure, which is equal to 0.0125 here.

$$\therefore \chi_2 = 0.0125$$

The relation between m and χ is:

$$m = \frac{\chi_2 \times 1000}{\chi_1 \times Mw_1} = \frac{0.0125 \times 1000}{(1 - 0.0125) \times 18} \begin{bmatrix} Mw_{\text{(H}_2\text{O})} \\ = 18 \text{ g mol}^{-1} \end{bmatrix}$$
$$= \frac{0.0125 \times 1000}{0.9875 \times 18} = 0.70$$

$$m = 0.70$$

ILLUSTRATION 2.76

A current of air was bubbled through a bulb containing 7.5 g of an organic subsance in 75 g of H₂O, then through pure water and finally through a U-tube containing fused CaCl2. The loss in the weight of the first tube was 2.81 g and the gain in the weight of U-tube was 2.864 g. Calculate the molecular weight of organic substance.

Sol. (Ostwald and Walker's method)

- **a.** Loss in weight of first bulb containing solvent (let W_1) is $W_1 \propto P_s$
- b. Loss in weight of second bubble containing solvent (let W_2) is $W_2 \propto P^\circ - P_S$.
- **c.** Gain in weight of CaCl₂ tube $(W_1 + W_2)$ is $W_1 + W_2 \propto P_S + P^\circ - P_S$

$$W_1 + W_2 \propto P^\circ$$

$$P^\circ - P_S = 2.864 - 2.81 = 0.054$$

$$\therefore \frac{P^{\circ} - P_{\rm S}}{P^{\circ}} = \frac{W_2}{W_1 + W_2}$$

$$\frac{0.054}{2.864} = \frac{7.5}{\frac{Mw_2}{75/18}} \Rightarrow Mw_2 = 95.46$$

ILLUSTRATION 2.77

At 25°C, the vapour pressure of pure water is 25.0 mm Hg and that of an aqueous dilute solution of urea is 20 mm Hg. Calculate the molality of the solution.

Sol. The given values are:

$$P_{\rm A}^{\circ} = 25$$
 mm Hg, $P_{\rm S} = 22$ mm Hg

$$m = ?$$

Using Raoult's law

$$\frac{P_{A}^{\circ} - P_{S}}{P_{A}^{\circ}} = \chi_{B}$$

Substituting all the values

$$\chi_{\rm B} = \frac{25 - 20}{25} = 0.20$$

$$\therefore \chi_A = 1 - \chi_B = 1 - 0.2 = 0.8$$

The relationship between molality and mole fraction of solute in a dilute solution is

$$m = \frac{\chi_B}{\chi_A M w_A} \times 1000, \text{ where } M w_A = \text{molar mass of solvent}$$
$$= \frac{0.2 \times 1000}{0.8 \times 18} = 13.8$$

Molality of solution is 13.8.

ILLUSTRATION 2.78

Equal amounts of a solute are dissolved in equal amounts of two solvents A and B. The lowering of vapour pressure for solution A has twice the lowering of vapour pressure for solution B. If Mw_A and Mw_B are the molecular weights of solvents A and B, respectively, then

$$\mathbf{a.} \quad Mw_{\mathbf{A}} = Mw_{\mathbf{B}}$$

b.
$$Mw_{\rm A} = Mw_{\rm B}/2$$

c.
$$Mw_A = 4Mw_B$$

$$\mathbf{d.} \ Mw_{\mathbf{A}}^{\mathbf{A}} = 2Mw_{\mathbf{B}}$$

Sol. d. Let solute (i) is added to solvents A and B.

$$\frac{P_i^{\circ} - P_{S}}{P_i^{\circ}} = \chi_i \approx \frac{Mw_{A}}{Mw_{i}}$$

$$\frac{P_i^{\circ} - P_{\rm S}}{P_i^{\circ}} = \chi_i \approx \frac{M w_{\rm B}}{M w_{\rm i}}$$

Given that lowering for solution A is twice to B

$$\therefore \frac{Mw_{\rm A}}{Mw_{\rm i}} = 2\left(\frac{Mw_{\rm B}}{Mw_{\rm i}}\right) \Rightarrow Mw_{\rm A} = 2Mw_{\rm B}$$

ILLUSTRATION 2.79

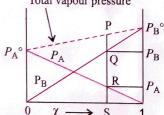
Consider the following vapour pressure- composition graph. SP is equal to:

a.
$$PQ + RS$$

$$b. PQ + QR$$

$$\mathbf{d.} \ PO + OR + RS$$

Total vapour pressure



Sol. c. According to Dalton's rule: Total pressure of a gaseous solution is equal to the sum of partial pressure,

$$P_{\text{total}} = P_{A} + P_{B}$$
$$= SR + SO$$

2.10.2 ELEVATION IN BOILING POINT

A liquid starts boiling when its vapour pressure becomes equal to the external pressure. The temperature at which this occurs is known as the boiling point of the liquid. If the external pressure is 1 atm, this temperature is known as the normal boiling point of the liquid. When a non-volatile solute is added to a liquid solvent the vapour pressure of the solution becomes comparatively smaller than that of the pure solvent (Raoult's law). Consequently the temperature at which the vapour pressure of solution becomes

equal to the external pressure, will be greater than that of pure equal to the external purpose of purpose of purpose of purpose of purpose of the solvent, thus raising its boiling point. As we know that the decrease in vapour pressure is directly proportional to the mole fraction of the solute in the solution, it is therefore expected that the corresponding increase in the boiling point also depends on the amount fraction of the solute in the solution.

The elevation in boiling point on the addition of a n_{0h} volatile solute to a solvent can be easily illustrated graphically in Fig. 2.17.

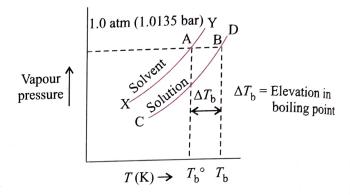


Fig. 2.17 Elevation in boiling point

Figure 2.17 shows the variation of vapour pressure with rise in temperature for solvent and solution. The curve XY gives the variation in vapour pressure for pure solvent and the curve CD gives the variation of vapour pressure for solution at different temperature. The curve CD lies below to XY because the vapour pressure of the solution is less than that of the pure solvent a all temperatures.

It is clear from the figure that at atmospheric pressure 1 am the curve of vapour pressure for solvent XY and for solution CD intersect at A and B. A and B on temperature axis correspond to boiling point of pure solvent (T_b°) and boiling point of solution $(T_{\rm b})$, respectively.

Thus, the boiling point of pure solvent T_b° is lower than that of solution (T_b) . Hence there is an elevation or increase in the boiling temperature of the solution as compared to that of the solvent.

The boiling point elevation depends on the amount of solute and experimentally it has been shown that the elevation in boiling point is directly proportional to the molal concentration of the solute in the solution.

i.e.,
$$\Delta T_{\rm b} \propto m \text{ or } \Delta T_{\rm b} = K_{\rm b} m$$
 ...(i)

Here m (molality) is the number of moles of solute in $1 \frac{1}{2}$ of solvent and the constant K_b is called *boiling point elevation* constant (or ebullioscopic constant). The unit of K_b is K kg mol

DERIVATION FOR THE ELEVATION IN BOILING POINT

The elevation in boiling point (ΔT_b) ,

 $\Delta T_{\rm b}$ = Boiling point of solution – Boiling point of pure solven

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions of different concentrations. The curve of the solutions is always below the curve of the pure solvent. T_0 , T_1 , and T_2 represent the boiling points of the boiling points of pure solvent, solution I, and solution I, respectively. The vapour pressure of pure solvent, solution I, and respectively. Solution II at temperature T_0 are P° , P_1 , and P_2 , respectively.

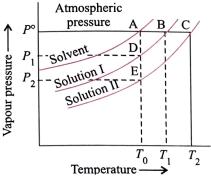


Fig. 2.18 Vapour-pressure-temperature curves

Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus, ΔACE and ΔABD are similar.

$$\therefore \frac{AC}{AB} = \frac{AE}{AD}$$
or
$$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P^{\circ} - P_2}{P^{\circ} - P_1}$$
or
$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$
or
$$\Delta T \propto \Delta P$$

From Raolut's law for dilute solution,

$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \frac{W_{B} \times Mw_{A}}{Mw_{B} \times W_{A}}$$

$$(P_{S} = vapour pressure O$$

$$(P_{S} = \text{vapour pressure of solution})$$
or $P^{\circ} - P_{S} = \frac{W_{B} \times Mw_{A}}{Mw_{B} \times W_{A}} P^{\circ}$

For the pure solvent, P° (its vapour pressure at the boiling point) and Mw_A (its molecular mass) are constant.

...
$$P^{\circ} - P_{s} \propto \frac{W_{B}}{Mw_{B}W_{A}}$$

or $\Delta P \propto \Delta T \propto \frac{W_{B}}{Mw_{B}W_{A}}$
or $\Delta T = K \cdot \frac{W_{B}}{Mw_{B}W_{A}}$...(i)

where K is a constant, called as elevation constant.

When
$$\frac{W_B}{Mw_B} = 1$$
, (one mole of solute) and $W_A = 1000$ g, then

$$\Delta T = \frac{K}{1000} = K_{\rm b}$$

where K_b is called molal elevation constant. It is defined as the elevation in boiling point produced when 1 mole of the solute is dissolved in 1000 g of the solvent.

Thus,
$$K = 1000K_{\rm b}$$

Putting this values in Eq. (i)

$$\Delta T^* = \frac{1000 K_b W_B}{M w_B W_A} \qquad ...(ii)$$
or $\Delta T = \text{Molality} \times K_b$

Since
$$\frac{W_{\rm B}}{Mw_{\rm B} \times W_{\rm A}} \times 1000 = \text{Molality}$$

The elevation the boiling point of a solution of non-electrolyte is proportional to its molality and equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raolut's laws of elevation in boiling point.

MOLAL ELEVATION CONSTANT AND ENTHALPY OF VAPOURIZATION

The molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_{\rm b} = \frac{Mw_{\rm A}RT_{\rm b}^2}{\Delta_{\rm vap}H \times 1000}$$
 or $K_{\rm b} = \frac{RT_{\rm b}^2}{l_{\nu} \times 1000}$

where Mw_A is the molar mass of solvent, T is the boiling point of solvent, R is the gas constant, and $\Delta_{\text{vap}}H$ is the molar enthalpy of vapourization of the solvent. l_v is the latent heat of vapourization.

Following are the experimental methods for the determination of the elevation in boiling point (ΔT_{h}) :

- a. Beckmann's method
- **b.** Cottrell's method

ILLUSTRATION 2.80

2 g each of two solutes A and B (molar mass of A is greater than that of B) are dissolved separately in 50 g each of the same solvent. Which will show greater elevation in the boiling point?

The solution containing solute B will show greater elevation in the boiling point because $\Delta T_{\rm b} \propto \frac{1}{M_{\rm bo}}$.

ILLUSTRATION 2.81

Distinguish between the boiling point of a liquid and the normal boiling point of a liquid.

Sol. The boiling point is the temperature at which the vapour pressure of the liquid becomes equal to the surrounding pressure. The normal boiling point is the temperature at which the vapour pressure is 1 atm.

ILLUSTRATION 2.82

Explain why the melting point of a substance gives an indication of the purity of a substance.

Sol. Impurities cause depression in freezing point (melting point). More the impurities, lower is the freezing point.

ILLUSTRATION 2.83

What happens to the vapour pressure of water if a table spoon of sugar is added to it?

Sol. Addition of non-volatile solute lowers the vapour pressure of solvent (water).

Define molal elevation constant or ebullioscopic constant.

Molal elevation constant is defined as the elevation in boiling point that takes place when the molality of solutions is unity.

ILLUSTRATION 2.85

Two liquids A and B boil at 130°C and 160°C, respectively. Which of the them has higher vapour pressure at 80°C.

Liquid A with lower boiling point is more volatile and therefore will have higher vapour pressure.

ILLUSTRATION 2.86

Match the following if the molar mass of X, Y, and Z are same:

Solvent	T _b (°C)	K _b (kg K mol ⁻¹)
X	127	0.73
Y	27	0.53
Z	253	0.98

Sol. Since
$$K_b = \frac{RT_b^2}{1000\Delta_{\text{vap}}H/Mw_{\text{solvent}}}$$
, we have

$$K_{\rm b} = \frac{RT_{\rm b}}{1000 \left(\frac{\Delta_{\rm vap}H}{T_{\rm b}}\right) / Mw_{\rm solvent}} = \text{(constant) } T_{\rm b}$$

$$\left[\frac{\Delta_{\text{vap}}H}{T_{\text{b}}} \text{ is taken to be constant as per Truton's rule}\right]$$

$$\Rightarrow K_{\rm b} \propto T_{\rm b}$$

Thus, we have

$$K_b(X) = 0.73 \text{ kg K mol}^{-1}; K_b(Y) = 0.531 \text{ kg K mol}^{-1};$$

 $K_b(Z) = 0.98 \text{ kg K mol}^{-1}$

ILLUSTRATION 2.87

The boiling point of a solution made by dissolving 12.0 g of glucose in 100 g of water is 100.34°C. Calculate the molecular weight of glucose; K_b for water = 0.52°C/m.

Sol. Using the relation for the molecular weight of a solute from elevation in boiling point, we have

$$Mw_{\rm B} = K_{\rm b} \left(\frac{W_{\rm B}}{W_{\rm A} \Delta T_{\rm b}} \times 1000 \right)$$

= $0.52 \left(\frac{12}{100 \times 0.34} \times 1000 \right)$
 $(\Delta T_{\rm b} = 100.34 - 100 = 0.34^{\circ}\text{C})$
 $\Rightarrow Mw_{\rm B} = 183.5 \text{ g mol}^{-1}$

ILLUSTRATION 2.88

A solution containing 0.2563 g of naphthalene (molecular mass = 128) in 50 g of carbon tetrachloride yields a boiling point elevation of 0.201°C while a solution of 0.6216 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.647°C. Find the molecular mass of unknown solute.

Sol. We know that

$$K_{b} = \frac{\Delta T_{b} \times W_{1} \times Mw_{2}}{1000 \times W_{2}}$$
For CCl₄; $K_{b} = \frac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$

$$Mw_{2} = \frac{1000 \times K_{b} \times W_{2}}{\Delta T_{b} \times W_{1}}$$

$$= \frac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44$$

ILLUSTRATION 2.89

The boiling point elevation constant for benzene is 2.57°C/m. The boiling point of benzene is 81.0°C. Determine the boiling point of a solution formed when 5 g of $C_{14}H_{12}$ is dissolved in 15 g of benzene.

Sol. Given weight of $C_{14}H_{12}(W_R) = 5 g$

Weight of benzene $(W_{\Delta}) = 15 \text{ g}$

$$\Delta T_{\rm b} = K_{\rm b} \left[\frac{\frac{W_{\rm B}}{M w_{\rm B}} \times 1000}{W_{\rm A}} \right]$$
$$= 2.57 \left[\frac{\frac{5}{180} \times 1000}{15} \right] = 4.76^{\circ} \text{C}$$

Now, $\Delta T_b = T_b - T_b^{\circ} \begin{bmatrix} T_b^{\circ} = \text{boiling point of pure solvent} \\ T_b^{\circ} = \text{boiling point of solution} \end{bmatrix}$

$$T_{b} = \Delta T_{b} + T_{b}^{\circ}$$
= 4.76 + 81.0
= 85.76°C

ILLUSTRATION 2.90

12.2 g of benzoic acid is dissolved in (i) 1 kg acetone ($K_b = 1.9 \text{ K}$ kg mol⁻¹) and (ii) 1 kg benzene ($K_b = 2.6 \text{ K kg mol}^{-1}$). The elevations of boiling points are 0.19°C and 0.13°C, respectively.

- a. What are the molar masses of benzoic acid in the two solutions?
- What are the structures of benzoic acid in the two solutions?

Solutions Let $Mw_{\rm B}$ be the molar mass of benzoic acid in the two solutions.

The molality of the solution is:

$$m = \frac{n_{\rm B}}{W_{\rm A}} = \frac{(12.2 \text{ g}) / Mw_{\rm B}}{1 \text{ kg}}$$

a. i. Acetone solution

$$0.19 \text{ K} = (1.9 \text{ K kg mol}^{-1}) \left[\frac{12.2 \text{ g/Mw}_{\text{benzoic acid}}}{1 \text{ kg}} \right]$$

$$Mw_{\text{benzoic acid}} = \frac{1.9 \times 12.2}{0.19} \text{ g mol}^{-1} = 122 \text{ g mol}^{-1}$$

ii. Benzene solution

$$0.13 \text{ K} = (2.6 \text{ K kg mol}^{-1}) \left[\frac{12.2 \text{ g/Mw}_{\text{benzoic acid}}}{1 \text{ kg}} \right]$$
$$Mw_{\text{benzoic acid}} = \frac{2.6 \times 12.2}{0.13} \text{ g mol}^{-1} = 244 \text{ g mol}^{-1}$$

b. The actual molar mass of benzoic acid (C₆H₅COOH) is 122 g mol⁻¹. This means benzoic acid is present as a monomer in acetone solution while it dimerizes in benzene solution. The structure of dimerized benzoic acid is

ILLUSTRATION 2.91

The ebullioscopic constant for benzene is 2.52 K m⁻¹. A solution of an organic substance in benzene boils at 0.125°C higher than benzene. Calculate the molality of solution?

Sol. Given values are:

$$K_{\rm b} = 2.52 \text{ K m}^{-1} \text{ or } 2.52 \text{ K kg mol}^{-1}$$

$$\Delta T_{\rm b} = 0.125$$
°C

Using the relation, $\Delta T_b = K_b m$

$$m = \frac{\Delta_b T}{K_b}$$
$$= \frac{0.125}{2.52} = 0.05$$

Hence, molality of the solution is 0.05 m.

ILLUSTRATION 2.92

18 g of glucose ($C_6H_{12}O_6$) is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil (at 1 atm)? K_b for water is 0.52 K kg mol⁻¹.

Sol. The given values are:

$$W_{\text{solute}} = 18 \text{ g}$$

$$W_{\text{solvent}} = 1 \text{ kg}$$

$$K_{\rm b} = 0.52 \text{ K kg mol}^{-1}$$

First we calculate elevation in the boiling point of solution.

$$\Delta T_{b} = \frac{K_{b} \times W_{\text{solute}}}{Mw_{\text{solute}} \times W_{\text{solvent}}}$$
$$= \frac{0.52 \times 18}{180 \times 1} = 0.052 \text{ K}$$

Since water boils at 373.15 K at 1 atm pressure, therefore the boiling point of solution will be

$$T_{\rm B} = T_{\rm b}^{\circ} + \Delta T_{\rm b} = 373.15 + 0.052 = 373.202 \text{ K}$$

Thus, the boiling point of solution is 373.202 K

ILLUSTRATION 2.93

0.90 g of a non-electrolyte was dissolved in 90 g of benzene. This raised the boiling point of benzene by 0.25°C. If the molecular mass of the non-electrolyte is 100.0 g mol⁻¹, calculate the molar elevation constant for benzene.

Sol. The given values are:

$$W_{\text{solute}} = 0.90 \text{ g}$$

$$W_{\text{solvent}} = 90.00 \text{ g}$$

$$\Delta T_{\rm b} = 0.25$$
°C

$$Mw_{\text{solute}} = 100.0 \text{ g mol}^{-1}$$

$$K_{\rm b} = ?$$

Using the formula

$$K_{\rm b} = \frac{\Delta T_{\rm b} \times W_{\rm solvent} \times Mw_{\rm solvent}}{1000 \times Mw_{\rm solute}}$$

$$\therefore K_{\rm b} = \frac{0.25 \times 100 \times 90.0}{1000 \times 0.90} = 2.5 \text{ K m}^{-1}$$

Thus, K_h is 2.5 K m⁻¹.

ILLUSTRATION 2.94

The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. $(K_b$ for benzene is 2.53 K kg mol⁻¹)

Sol. Given values are:

$$T_{\text{(benzene)}}^{\circ} = 353.00 \text{ K}; K_{\text{b}} = 2.53 \text{ K kg mol}^{-1}$$

$$T_{\rm b(solution)} = 354.00 \text{ K}$$

$$W_{\text{solute}} = 1.80 \text{ g}$$

$$W_{\text{solvent}} = 90 \text{ g}$$

The elevation in boiling point,
$$\Delta T_b = T_{b(\text{solution})} - T_b^{\circ}_{(\text{solvent})}$$

Molar mass of solute is given as

$$Mw_{\text{solute}} = \frac{K_{\text{b}} \times 1000 \times W_{\text{solute}}}{\Delta T_{\text{b}} \times W_{\text{solvent}}}$$

$$Mw_{\text{solute}} = \frac{2.53 \times 1000 \times 1.80}{0.88 \times 90} = 58.0 \text{ g mol}^{-1}$$

Hence, the molar mass of solute is 58.0 g mol⁻¹.

ILLUSTRATION 2.95

Calculate the molar mass of a substance 1 g of which when dissolved in 100 g of water gave a solution boiling at 100.1°C at a pressure of 1 atm (K_b for water = 0.52 K kg mol⁻¹)

Sol. The given values are

$$W_{\rm B} = 1 \text{ g ; } K_{\rm b} = 0.52 \text{ K kg mol}^{-1}$$

$$W_{\rm A} = 100 {\rm g}$$

$$\Delta T_{\rm h} = 100.1 - 100 = 0.1$$

Using the equation

$$Mw_{\rm B} = \frac{K_{\rm b} \times W_{\rm B}}{\Delta T_{\rm b} \times W_{\rm A}}$$

Substituting all values, we get

$$Mw_{\rm B} = \frac{0.52 \times 1 \times 1000}{0.1 \times 100 \,\text{g}} = 52$$

ILLUSTRATION 2.96

On dissolving 3.24 g of sulphur in 40 g of benzene, the boiling point of the solution was higher than that of benzene by 0.81 K. What is the molecular formula of sulphur? (K_b for benzene = $2.53 \text{ K kg mol}^{-1}$, atomic mass of sulphur = 32 g mol^{-1}).

Sol. The given values are:

$$W_{\rm B} = 3.24 \, \text{g}; \quad W_{\rm A} = 40 \, \text{g}$$

$$W_{\rm A} = 40$$
 §

$$W_{\rm B} = 3.24 \text{ g},$$
 $\Delta T_{\rm b} = 0.81 \text{ K}; K_{\rm b} = 2.53 \text{ K kg mol}^{-1}$

Using formula,

$$Mw_{\rm B} = \frac{K_{\rm b} \times 1000 \times W_{\rm B}}{\Delta T_{\rm b} \times W_{\rm A}}$$

On substituting all the values, we get

$$Mw_{\rm B} = \frac{2.53 \times 1000 \times 3.24}{0.81 \times 40} = 253$$

Let the molecular formula of sulphur = S_{ν}

Atomic mass of sulphur = 32

Molecular mass = $32 \times x$

$$32x = 253$$

$$x = \frac{253}{32} = 7.91 \approx 8$$

 \therefore Molecular formula of sulphur = S_8

ILLUSTRATION 2.97

A solution containing 12 g of a non-electrolyte substance in 52 g of water gave boiling point elevation of 0.40 K. Calculate the molar mass of the substance. $(K_b \text{ for water} = 0.52 \text{ K kg mol}^{-1})$

The given values are:

$$W_{\rm B} = 12 \text{ g: } W_{\rm A} = 52 \text{ g}$$

 $\Delta T_{\rm b} = 0.4 \text{ K}$

$$\Delta T_{\rm L} = 0.4 \text{ K}$$

Using the formula,

$$Mw_{\rm B} = \frac{K_{\rm b} \times W_{\rm B} \times 1000}{\Delta T_{\rm b} \times W_{\rm A}}$$

$$\therefore Mw_{\rm B} = \frac{0.52 \times 12 \times 1000}{0.4 \times 52} = 300$$

Molecular weight of solute is 300 g mol⁻¹.

ILLUSTRATION 2.98

Molal elevation constant (K_b) values of following alcohols are in the order:

 $CH_3CH_2CH_2CH_2OH > (CH_3)_2CH-CH_2OH > (CH_3)_3C-OH$ Explain in brief.

Sol Moving from CH₃CH₂CH₂CH₂OH to (CH₃)₃C-OH via (CH₂)₂CHCH₂OH, the branching increases, the surface area decreases resulting into decrease in van der Waal's force and hence boiling point,

$$K_{\rm b} = \frac{RT_{\rm b}^2 M w_{\rm A}}{1000 \rm H_{\rm v}},$$

molecular weight (Mw_A) remains the same for all three $alcoh_{0|_{R}}$ According to Trouton's rule, $\Delta_v H/T_b$ is almost constant for all the liquids of almost similar kind of association.

Thus,
$$\frac{RMw_AT_b}{1000H_v}$$
 is constant and $K_b \propto T_b$.

2.10.3 DEPRESSION IN FREEZING POINT

We know that at freezing point of a solvent, the solid and liquid are in equilibrium. This is possible only if they have same vapour pressure. Therefore, a solution will freeze when its vapour pressure becomes equal to the vapour pressure of the pure solid solvent. Thus, the freezing point is the temperature at which the solid and liquid states of the substance have same vapour pressure. According to Raoult's law, when a non-volatile solute is added to a solvent, its vapour pressure decreases. The lower vapour pressure of a solution causes the lowering of the freezing point compared to that of the pure solvent. This may be illustrated graphically as shown in Fig. 2.19.

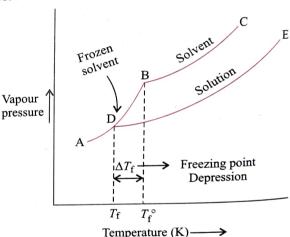


Fig. 2.19 Depression in freezing point

In the above figure, curve BC shows the variation of vapour pressure of pure solvent with temperature. The addition of not volatile solutes lowers the vapour pressure of solvent. Cunt DE shows the variations of vapour pressure of solution with temperature. Curve AB corresponds to the vapour pressure of the solid at different temperature.

Point B, where solid and liquid solvents meet (i.e., solid and liquid states have the same vapour pressure), corresponds to the temperature and a surfection of the same vapour pressure. temperature of freezing (T_f°) for pure solvent. The temperature corresponding to point D where the solid solvent and liquid solution most (i.e., i.e., and i.e., solution meet (i.e., solid and liquid states have the same vapout pressure) represents the freezing point temperature (T_i) of the solution solution.

From Fig. 2.19, it is clear that T_f is less than T_f° , this shows at the freezing temperature T_f° at the freezing temperature T_f° . that the freezing temperature of the solution is less than T_f , this pure solvent. The decrease of the solution is less than T_f , the pure solvent. pure solvent. The decrease in freezing point $\Delta T_{\rm f} = T_{\rm f}^{\circ} - T_{\rm f}^{\circ}$ known as depression in 6 known as depression in freezing point.

2.33

Similar to the elevation in boiling point, the depression in Similar (ΔT_f) for dilute solution is directly proportional freezing point (ΔT_f) of the solution The molality (m) of the solution.

$$\Delta T_{\rm f} \propto m \text{ or } \Delta T_{\rm f} = m \times K_{\rm f}$$
 ...(i)

Thus, The proportionality constant $K_{\rm f}$ which depends on the of the solvent is known as freezing point depression national and the second constant. The unit of K_f is K kg mol⁻¹.

Following are the experimental methods for the determination of the depression in freezing point (ΔT_e)

- a. Beckmann's method
- b. Rast's method

DERIVATION OF THE DEPRESSION IN FREEZING POINT

The difference between the freezing points of a pure solvent and its solution is called depression in freezing point.

 (ΔT) = Freezing point of the solvent – Freezing point of the solution

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions, solution I and solution II. CFB is a curve for solid solvent. The solvent, solution I, and solution II vapour pressure curves meet CFB curve at points B, F, and C, respectively. Thus, T_0 , T_1 , and I, are the freezing point of pure solvent, solution I, and solution II respectively. The solvent, solution I, and solution II are, thus, P° , P_{1} , and P_{2} , respectively (Fig. 2.20).

For very dilute solutions, curves FD and CE are almost straight lines and CB is also nearly a straight line. \triangle BEC and \triangle BDF are similar.

$$S_0 \frac{EC}{DF} = \frac{BE}{BD}$$

or
$$\frac{T_0 - T_2}{T_0 - T_1} = \frac{P^\circ - P_2}{P^\circ - P_1}$$

or
$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$
 or $\Delta T \propto \Delta P$

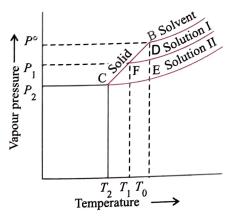


Fig. 2.20

From Raoult's law for dilute solutions,

$$\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} = \frac{W_{\rm B} M w_{\rm A}}{M w_{\rm B} W_{\rm A}}$$

or
$$P^{\circ} - P_{S} = \frac{W_{B}Mw_{A}}{Mw_{B}W_{A}}P^{\circ}$$

For the pure solvent, P° and Mw are constant.

$$P^{\circ} - P_{S} \propto \frac{W_{B}}{Mw_{B} \times W_{A}}$$
or
$$\Delta P \propto \frac{W_{B}}{Mw_{B} \times W_{A}}$$
or
$$\Delta P \propto \Delta T \propto \frac{W_{B}}{Mw_{B} \times W_{A}}$$
or
$$\Delta T = K \cdot \frac{W_{B}}{Mw_{B} \times W_{A}} \qquad ...(i)$$

where K is a constant called depression constant.

When
$$\frac{W_B}{Mw_B} = 1$$
 (one mole of solute) and $W_A = 1$ g

If
$$\frac{W_{\rm B}}{Mw_{\rm B}} = 1$$
 and $W_{\rm A} = 1000$ g

$$\Delta T = \frac{K}{1000} = K_{\rm f}$$

where K_f is called molal depression constant. It is defined as the depression in freezing point produced when 1 mol of solute is dissolved in 1000 g of the solvent.

Thus,
$$K = 1000K_{\rm f}$$

Putting this value in Eq. (i), we get

$$\Delta T^* = 1000 K_{\rm f} \frac{W_{\rm B}}{M w_{\rm B} W_{\rm A}}$$

or
$$\Delta T = \text{Molality} \times K_{\text{f}}$$

RELATION BETWEEN MOLAL DEPRESSION **CONSTANT AND ENTHALPY OF FUSION**

 $K_{\rm f}$ is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_{\rm f} = \frac{Mw_{\rm A}RT_{\rm f}^2}{\Delta_{\rm fis}H \times 1000} \text{ or } K_{\rm f} = \frac{RT_{\rm f}^2}{l_{\rm f} \times 1000}$$

where Mw_A is the molar mass of solvent, T_f is the freezing point of solvent, $\Delta_{\text{fus}}H$ is the molar enthalpy of fusion of the solvent, R is the gas constant, and l_f is the latent heat of fusion.

Determination of Depression in Freezing Point

In case of depression of freezing point determination

Case (a): When water as solvent is in excess, remaining water will separate out as ice. Refer Illustrations 2.135 and 2.136.

Case (b): When solute is in excess, remaining solute will precipitate. Refer Illustration 2.137.

ILLUSTRATION 2.99

Why is it advised to add ethylene glycol to water in car radiator while driving in a hill station?

Ethylene glycol lowers the freezing point of water, and therefore, it does not freeze in a hill station.

Sodium chloride solution freezes at lower temperature than water but boils at higher temperature than water. Explain.

The freezing point of a liquid depresses on the addition of a non-volatile solute, and therefore, a solution of sodium chloride freezes at a temperature lower than the freezing point of water. On the other hand, there is elevation of boiling point on the addition of a non-volatile solute and consequently the boiling point of sodium chloride solution is more than that of water.

ILLUSTRATION 2.101

Why is camphor preferred as a solvent for measuring the molecular mass of naphthalene by Rast method?

Sol. Camphor has a large K_f value (39.8°), and therefore, it causes large depression in the melting point of a solution with very small amount of solute (naphthalene).

ILLUSTRATION 2.102

Sodium chloride or calcium chloride is used to clear snow from the roads. Why?

Sodium chloride depress the freezing point of water to such an extent that it cannot freeze to form ice. Therefore, it melts off easily at the prevailing temperature.

ILLUSTRATION 2.103

Define molal depression constant or cryoscopic constant.

It is the depression in freezing point when 1 mol of a non-volatile solute is dissolved in 1000 g of a solvent.

ILLUSTRATION 2.104

What is an antifreeze?

Sol. A substance (such as ethylene glycol) which is added to water to lower its freezing point is called an antifreeze. It is so named because it delays freezing.

ILLUSTRATION 2.105

What are units of cryoscopic constant?

K kg mol⁻¹. Sol.

ILLUSTRATION 2.106

What is de-icing agent? How does it work?

Common salt is called de-icing agent as it lowers the freezing point of water to such an extent that it does not freeze to form ice. Thus, it is used to clear snow from roads.

ILLUSTRATION 2.107

What do you understand by the term that K_f for water is 1.86 K kg mol⁻¹?

Sol. It means that the freezing point of water is lowered had a solute is discoluted by 1.86 K when 1 mol of a non-volatile solute is dissolved in 10% g of water.

ILLUSTRATION 2.108

Calculate the molal depression constant of a solvent which has

- a. Freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1} .
- b. Freezing point 20.0°C and latent heat of fusion 200.00 J g^{-1} .

...(i)

Sol. a.
$$K_f = \frac{RT_f^2}{1000 \times l_f}$$

 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $T_f = 16.6 \text{°C} = 273 + 16.6 = 289.6 \text{ K}$
 $l_f = 180.75 \text{ J g}^{-1}$

Substituting the values in Eq. (i), we get

$$K_{\rm f} = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86$$

b.
$$K_f = \frac{RT_f^2}{1000 \times l_f}$$

 $T_f = 273 + 20.0 = 293.0$
 $l_f = 200.0 \text{ J g}^{-1} = \frac{8.314 \times (293.0)^2}{1000 \times 200.0} = 3.56$

ILLUSTRATION 2.109

If the boiling point of an aqueous solution containing a nonvolatile solute is 100.15°C. What is its freezing point? Given latent heat of fusion and vapourization of water 80 cal g-1 and 540 cal g⁻¹, respectively.

Sol. For a given aqueous solution,

For a given aqueous solution, ...(i)
$$\Delta T_{\rm f} = K_{\rm f} \times m$$
 ...(ii)
$$\Delta T_{\rm b} = K_{\rm b} \times m$$

$$K_{\rm f} = \frac{RT_{\rm f}^2}{1000 \, l_{\rm f}}$$
 ...(iii)

$$K_{\rm b} = \frac{RT_{\rm b}^{\ 2}}{1000 \, l_{\rm v}} \tag{iv}$$

Dividing Eq. (iii) by Eq. (iv),

Dividing Eq. (iii) by Eq. (iv),

$$\frac{K_f}{K_b} = \frac{T_f^2 \times l_v}{T_b^2 \times l_f}$$

$$\therefore \frac{\Delta T_f}{\Delta T_b} = \frac{T_f^2 \times l_v}{T_b^2 \times l_f}$$

$$T_f = 0 + 273 = 273 \text{ K},$$

$$T_b = 100 + 273 = 373 \text{ K}$$

$$l_f = 80 \text{ cal g}^{-1}, l_v = 540 \text{ cal g}^{-1}$$

$$\therefore \frac{\Delta T_f}{0.15} = \frac{273 \times 273 \times 540}{373 \times 373 \times 80}$$
or
$$\Delta T_f = \frac{273 \times 273 \times 540}{373 \times 373 \times 80} \times 0.15 = 0.542$$

$$\therefore T_f = 0 - 0.542 = -0.542^{\circ}\text{C}$$

ILLUSTRATION 2.110 1.4g of acetone dissolved in 100 g of benzene gave a solution 1.4g of access at 277.12 K. Pure benzene freezes at 278.4 K. which freezes at 278.4 K. which freezes at 278.4 K. which freezes at 278.4 K. as of solid (A) dissolved in 100 g of benzene gave a solution 18 of some at 277.76 K. Calculate the molecular mass of (A).



We know that
$$\Delta T = K_f \times \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

where ΔT = Depression in freezing point

 $K_f = Molal$ depression constant of benzene

w, = Mass of solute

 Mw_2 = Molecular mass of solute

W = Mass of solvent

 C_{ase} 1: $(278.4 - 277.12) = K_f \times \frac{1.4 \times 1000}{58 \times 100}$

$$1.28 = K_{\rm f} \times \frac{14}{58} \qquad ...(i)$$

Case II:
$$(278.4 - 277.76) = K_f \times \frac{2.8 \times 1000}{Mw_A \times 100}$$

$$0.64 = K_{\rm f} \times \frac{28}{Mw_{\rm A}} \qquad \dots (ii)$$

Dividing Eq. (i) by Eq. (ii), we get

$$Mw_A = 232$$

LLUSTRATION 2.111

The freezing point of a solution containing 50 cm³ of ethylene glycol in 50 g of water is found to be -34°C. Assuming ideal behaviour, calculate the density of ethylene glycol (K_f for water $= 1.86 \text{ K kg mol}^{-1}$).



$$\Delta T = \frac{K_{\rm f} \times W_2 \times 1000}{Mw_2 \times W_1}$$

$$34 = 1.86 \times \frac{W_2 \times 1000}{62 \times 50}$$

$$W_2 = 56.66 \text{ g}$$

$$V = \frac{W_2}{d}$$

$$50 = \frac{56.66}{d}$$

$$d = 1.13 \text{ g cm}^{-3}$$

ILLUSTRATION 2.112

An aqueous solution of a non-volatile solute boils at 100.17°C. At what temperature will the solution freeze? (Given: $K_b = 0.512$ and $K_{\rm f} = 1.86$)



Sol. We know that

$$\Delta T_{\rm b} = \text{Molality} \times K_{\rm b}$$

$$0.17 = Molality \times 0.512$$

Molality of the solution =
$$\frac{0.17}{0.512}$$
 m

Let depression in freezing point be $\Delta T_{\rm f}$

$$\Delta T_f = \text{Molality} \times K_f$$
$$= \frac{0.17}{0.512} \times 1.86 = 0.62^{\circ}\text{C}$$

Thus, the freezing point of the solution is

$$0.00 - 0.62 = -0.62$$
°C

ILLUSTRATION 2.113

A solution of urea in water has boiling point of 100.15°C. Calculate the freezing point of the same solution if $K_{\rm f}$ and $K_{\rm b}$ for water are 1.87 K kg mol⁻¹ and 0.52 K kg mol⁻¹, respectively.

Sol.
$$\Delta T_{\rm b} = (100.15 - 100) = 0.15^{\circ} \text{C}$$

We know that $\Delta T_h = \text{Molality} \times K_h$

Molality =
$$\frac{\Delta T_b}{K_b} = \frac{0.15}{0.50} = 0.2884$$

$$\Delta T_f = \text{Molality} \times K_f$$

= 0.2884 × 1.87
= 0.54°C

Thus, the freezing point of the solution = -0.54°C

ILLUSTRATION 2.114

By dissolving 13.6 g of a substance in 20 g of water, the freezing point decreased by 3.7°C. Calculate the molecular mass of the substance. (Molal depression constant for water = 1.863 K kg mol^{-1})

Sol.
$$Mw_2 = \frac{1000K_f \times W_2}{W_1 \times \Delta T}$$

Given, $K_s = 1.863 \text{ K kg mol}^{-1}$

$$W_2 = 13.6 \text{ g}, W_1 = 20 \text{ g}, \Delta T = 3.7^{\circ}\text{C}$$

$$Mw_2 = \frac{1000 \times 1.863 \times 13.6}{20 \times 3.7} = 342.39$$

ILLUSTRATION 2.115

On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density 0.8 g mL⁻¹), its freezing point decreases by 0.25°C. Calculate the molecular mass of non-volatile substance $(K_c = 5.1 \text{ K kg mol}^{-1})$

Mass of benzene, $W = Volume \times Density$

$$= 30 \times 0.8 = 24 \text{ g}$$

Given,
$$K_f = 5.12 \text{ K kg mol}^{-1}$$
, $W_2 = 0.25 \text{ g}$
 $\Delta T = 0.25^{\circ}\text{C}$,

We know that

$$Mw_2 = \frac{1000K_f \times W_2}{W_1 \times \Delta T}$$
 (substituting all values)
= $100 \times 5.12 \times 0.25$ = 213.23

$$=\frac{100\times5.12\times0.25}{24\times0.25}=213.33$$

ILLUSTRATION 2.116

In a cold climate water gets frozen causing damage to radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at -6° C. (K_f for water = 1.85 K kg mol⁻¹)

Sol. Given,

Given,

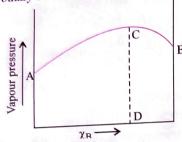
$$\Delta T = 6^{\circ}\text{C}, W_2 = 4 \text{ kg} = 4000 \text{ g}, Mw_2 = 62, K_f = 1.85$$

$$W_2 = \frac{Mw_2 \times W_1 \times \Delta T}{1000 \times K_f}$$

$$= \frac{62 \times 4000 \times 6}{1000 \times 1.85} = 804.32 \text{ g}$$

ILLUSTRATION 2.117

The diagram given below is a vapour- pressure-composition diagram for a binary solution of A and B.



In the solution, A-B interactions are:

- a. Similar to A-A and B-B interactions
- b. Greater than A-A and B-B interactions
- Smaller than A-A and B-B interactions
- Unpredictable

Sol. c. The solution is showing positive deviation from Raoult's law. Therefore interaction between A-A and B-B is smaller than A-B interaction.

ILLUSTRATION 2.118

1.355 g of a substance dissolved in 55 g of CH₃COOH produced a depression in the freezing point of 0.618°C. Calculate the molecular weight of the substance $(K_f = 3.85)$

Sol.
$$\Delta T = K_{\rm f} \frac{W_{\rm B} \times 1000}{Mw_{\rm B} \times W_{\rm A}}$$

where $W_{\rm B}$ = mass of solute, $Mw_{\rm B}$ = molar mass of solute, W_{A} = mass of solvent

$$0.618 = 3.85 \times \frac{1.355 \times 1000}{Mw_{\rm B} \times 55}$$

$$Mw_{\rm B} = 153.47$$

ILLUSTRATION 2.119

What mass of sugar $C_{12}H_{22}O_{11}(M_0 = 342)$ must be dissolved in 4.0 kg of H₂O to yield a solution that will freeze at -3.72°C. $(Take K_{\epsilon} = 1.86^{\circ} C m^{-1})$

Sol
$$\Delta T_f = 3.72$$
°C $Mw_{\text{sugar}} = 342$

$$\Delta T_{\rm f} = 3.72 \cdot \text{C } M W_{\text{sugar}} - 342$$

$$\Delta T_{\rm f} = K_{\rm f} \left[\frac{W_{\rm B}}{M w_{\rm B}} \times 1000 \right]$$

$$\Rightarrow W_{\rm B} = \frac{\Delta_{\rm f} T W_{\rm A} M w_{\rm B}}{1000 K_{\rm f}}$$

$$\Rightarrow W_{\rm B} = \frac{3.72 \times 4 \times 10^3 \times 342}{1000 \times 1.86} = 2736 \text{ g}$$

ILLUSTRATION 2.120

Calculate the freezing point depression and boiling point elevation of a solution of 10.0 g of urea ($M_{\rm B} = 60$) in 50.0 g of water at 1 atm. pressure. K_b and K_f for water 0.52°C m⁻¹ and 1.86°C m⁻¹ respectively.

Sol. Depression in freezing point = ΔT_f and elevation in b_{0il} $ing point = \Delta T_h$

$$\Delta T_{\rm f} = K_{\rm f} \left(\frac{W_{\rm B}}{Mw_{B}} \times 1000 \right) = 1.86 \left(\frac{10}{60} \times 1000 \right) = 6.2^{\circ} \text{C}$$

$$\Delta T_{\rm b} = K_{\rm b} \left(\frac{\overline{W_{\rm B}}}{\overline{Mw_{\rm B}}} \times 1000 \right) = 0.52 \left(\frac{10}{60} \times 1000 \right) = 1.7^{\circ} \text{C}$$

Freezing point
$$(T_f) = T_f^{\circ} - \Delta T_f = 0 - 6.2 = -6.2^{\circ}\text{C}$$

Boiling point $(T_b) = T_b^{\circ} + \Delta T_b = 100 + 1.7 = 101.7^{\circ}\text{C}$

ILLUSTRATION 2.121

1 g of monobasic acid in 100 g of water lowers the freezing point by 0.168°. If 0.2 g of same acid requires 15.1 mL molof N/10 alkali for complete neutralization, calculate the degree of dissociation of acid. K_f for H_2O is 1.86 K mol⁻¹ kg.

Sol.
$$\Delta T = \frac{1000 \times K_{\rm f} \times W_2}{Mw_2 \times W_1}$$

and $\Delta T = 0.168$, $W_2 = 1$ g, $W_1 = 100$ g and $K_f = 1.86$

$$\therefore Mw_{\text{acid}} = 110.71 \text{ (This is exp. mol. wt.)}$$

Now, mEq of acid = mEq of alkali

$$\frac{0.2}{E} \times 1000 = 15.1 \times \frac{1}{10}$$

:.
$$Ew$$
 of acid = $\frac{0.2 \times 1000 \times 10}{15.1} = 132.45$

$$\therefore \text{ Normal } Mw = 132.45 \times 1$$

(Since monobasic)

Now,
$$\frac{Mw_{\text{Normal}}}{Mw_{\text{Exp}}} = \frac{132.45}{110.71} = 1 + \alpha \implies \alpha = 19.6\%$$

ILLUSTRATION 2.122

How many grams of sucrose (molecular weight 342) should be discalled the control of the discalled the control of the control o be dissolved in 100 g water in order to produce a solution with 105°C difference between the freezing point and the boiling point $(K_{\rm b} = 0.51 \,{\rm ^{\circ}C}\ {\rm m^{-1}}, K_{\rm f} = 1.86 \,{\rm ^{\circ}C}\ {\rm m^{-1}})$

Sol. The given values are

$$W_{\text{solvent}} = 100 \text{ g}$$

$$Mw_{\text{solute}} = 342 \text{ g mol}^{-1}$$

$$T_{\rm b} - T_{\rm f} = 105.0$$
°C

Using the formula, $\Delta T_b = K_b m$ and $\Delta T_f = K_f m$

Freezing point of solution
$$(T_f) = 0 - \Delta T_f$$

$$= 0 - K_f m \qquad ...(i)$$

Subtracting Eq. (ii) from Eq. (i),

$$T_{\rm b} - T_{\rm f} = (100 + K_{\rm b}m) - (-K_{\rm f}m)$$

$$\frac{1}{105} = 100 + 0.51m + 1.86m$$

$$m = 2.11$$

00

eezine

molidegree

6

basic

Weight of sucrose to be dissolved in 100 g

$$= \frac{2.11 \times 342 \times 100}{1000} = 72.16 \,\mathrm{g}$$

ILLUSTRATION 2.123

A liquid possessing which of the following characteristics will be most suitable for determining the molecular mass of a compound by cryoscopic measurements?

- a. That having low freezing point and small enthalpy of
- b. That having high freezing point and small enthalpy of fusion
- c. That having high freezing point and small enthalpy of vapourization
- d. That having large surface tension
- Sol. b. K_f should be high so as to get a high value of ΔT_f

Now
$$K_{\rm f} \propto \frac{{T_{\rm f}}^2}{\Delta_{\rm vap} H}$$

ILLUSTRATION 2.124

45 g of ethylene glycol $C_2H_6O_2$ is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

Given $K_f = 1.86 \text{ K kg mol}^{-1}$.

Sol. Depression in freezing point is related to the molality, therefore the molality of the solution with respect to ethylene glycol,

$$\Delta T_{\rm f} = K_{\rm f} m$$

Mole of ethylene glycol =
$$45 \text{ g} \times \frac{1 \text{ mol}}{62 \text{ g}} = 0.73 \text{ mol}$$

Mass of water in kg =
$$600 \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.60 \text{ kg}$$

Hence, molality of ethylene glycol

$$= \frac{0.73 \text{ mol}}{0.60 \text{ kg}} = 1.20 \text{ mol kg}^{-1}$$

Therefore, freezing point depression

$$\Delta T_{\rm f} = 1.86 \text{ K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} = 2.2 \text{ K}$$

Freezing point of the aqueous solution

$$T_{\rm f} = T_{\rm f}^{\circ} - \Delta_{\rm f} T$$

= 273.15 K - 2.2 K = 270.95 K

ILLUSTRATION 2.125

1.0 g of non-electrolyte solute dissolved in 50.0 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 kg mol⁻¹. Find the molecular mass of the solute.

Sol. Given values are:

$$W_{\text{solute}} = 1.0 \text{ g}$$

$$W_{\text{solvent}} = 50.0 \text{ g}$$

$$\Delta T_{\rm f} = 0.40 \text{ K}$$

$$K_{\rm f} = 5.12 \text{ K kg mol}^{-1}$$

Substituting this value in equation

$$Mw_{\text{solute}} = \frac{K_{\text{f}} \times W_{\text{solute}} \times 1000}{\Delta T_{\text{f}} \times W_{\text{solvent}}}$$

$$= \frac{5.12 \text{ K kg mol}^{-1} \times 1.0 \times 1000}{0.40 \text{ K} \times 50.0 \text{ g}}$$

$$= 256.0 \text{ g mol}^{-1}$$

Thus, molecular mass of the solute = 256.0 g mol^{-1}

ILLUSTRATION 2.126

Addition of 0.40 g of a compound to 45.5 m L of benzene (density 0.879 g mL⁻¹) lowers the freezing point from 5.51°C to 4.998°C. If $K_{\rm f}$ for benzene is 5.12 K kg mol⁻¹, calculate the molar mass of the compound.

Sol. The given values are:

$$W_{\text{solute}} = 0.40 \text{ g}; K_{\text{f}} = 5.12 \text{ K m}^{-1}$$

$$\rho_{(benzene)}=0.879~g~mL^{-1}$$

$$V_{\text{(benzene)}} = 45.50 \text{ mL}$$

$$\Delta T_f = T_f^{\circ} - T_f = 5.51 - 5.03 = 0.512^{\circ}\text{C}$$

Now weight of benzene =
$$V \times \rho$$

$$=45.50 \times 0.879$$

$$=40.00 g$$

Molar mass of solute, $M_{\rm solute}$ is calculated as

$$Mw_{\text{solute}} = \frac{K_{\text{f}} \times W_{\text{solute}} \times 1000}{W_{\text{solvent}} \times \Delta T_{\text{f}}}$$
$$= \frac{5.12 \times 0.40 \times 1000}{40 \times 0.512} = 400$$

Thus, the molecular weight of solute is 400 g mol⁻¹.

ILLUSTRATION 2.127

- The molal freezing point depression constant of benzene (C_6H_6) is 4.90 K kg mol⁻¹. Selenium exists as a polymer of the type Se_x . When 3.26 g of selenium is dissolved in 226 g of benzene, the observed freezing point is 0.112°C lower than pure benzene. Deduce the molecular formula of selenium. (Atomic mass of $Se = 78.8 \text{ g mol}^{-1}$)
- Sol. The given values are:

$$K_{\rm f} = 4.90 \text{ K kg mol}^{-1}$$

$$W_{\rm solute} = 3.26 \, {\rm g}$$

$$W_{\text{solvent}} = 226 \text{ g}$$

 $\Delta T_{\text{f}} = 0.112 ^{\circ}\text{C}$

Now, molecular mass can be calculated as

$$Mw_{\text{solute}} = \frac{K_{\text{f}} \times W_{\text{solute}} \times 1000}{W_{\text{solvent}} \times \Delta T_{\text{f}}}$$
$$= \frac{4.901 \times 3.26 \times 1000}{226 \times 0.112} = 632 \text{ g mol}^{-1}$$

Now, molecular mass of $Se_x = x \times 78.8$

$$632 = x \times 78.8$$

or
$$x = \frac{632}{78.8} = 8$$

 \therefore Molecular formula of selenium = Se₈.

ILLUSTRATION 2.128

Two elements A and B form compounds having molecular formula AB_2 and AB_4 . When dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol⁻¹. Calculate the atomic mass of A and B.

Sol. Given values are:

$$W_{AB_2} = 1.0 \text{ g}; W_{benzene} = 20 \text{ g}$$

$$W_{AB} = 1.0 \text{ g}$$

$$\Delta T_{\rm f(AB_2)} = 2.3 \text{ K}$$

$$\Delta T_{\rm f(AB_a)} = 1.3 \text{ K}$$

Let us calculate the molar masses of AB₂ and AB₄.

For AB₂ compound

$$Mw_{\rm solute} = \frac{K_{\rm f} \times W_{\rm solute} \times 1000}{W_{\rm solvent} \times \Delta T_{\rm f}}$$

$$Mw_{AB_2} = \frac{5.1 \times 1.0 \times 1000}{20.0 \times 2.3} = 110.87 \text{ g mol}^{-1}$$

$$Mw_{AB_2} = 110.87 \text{ g mol}^{-1}$$

For AB₄ compound

$$Mw_{AB_4} = \frac{5.1 \times 1.0 \times 1000}{20.0 \times 1.3} = 196.15 \text{ g mol}^{-1}$$

Let α is the atomic mass of A and β is the atomic mass of B, then

$$Mw_{AB_2} = \alpha + 2\beta = 110.87$$
 ...(i)

$$Mw_{AB_4} = \alpha + 4\beta = 196.15$$
 ...(ii)

Subtracting Eq. (ii) from Eq. (i), we get

$$-2\beta = -85.28$$

$$\beta = 42.64$$

Substituting the value of β in Eq. (i),

$$\alpha + 2 \times 42.64 = 110.87$$

$$\alpha = 110.87 - 85.28 = 25.59$$

Atomic mass of A = 25.59

Atomic mass of B = 42.64

ILLUSTRATION 2.129

In a cold climate water gets frozen causing damages to the radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol the added to χ kg of water to prevent it from freezing at -8° C. $(K_f \text{ for } Water = 1.8 \text{ K m}^{-1})$

Sol. The given values are

$$W_{\rm A} = 2 \text{ kg} = 2 \times 10^3 \text{ g}; Mw_{\rm B} = 62 \text{ g mol}^{-1}$$

$$K_c = 1.8 \text{ K m}^{-1}$$

$$\Delta T_{\rm f} = 0 - (-8) = 8^{\circ}$$

Using formula,
$$W_{\rm B} = \frac{\Delta T_{\rm f} \times W_{\rm A} \times M w_{\rm B}}{K_{\rm f} \times 1000}$$

$$W_{\rm B} = \frac{8 \times 2 \times 10^3 \times 62}{1.8 \times 1000} = 551.1 \text{ g}$$

Therefore, the amount of ethylene glycol to be added is 551.11 g.

ILLUSTRATION 2.130

Two aqueous solution containing, respectively, 7 g urea (molar mass = 60 g) and 42 g of substance X in 100 g of water freeze at the same temperature. Calculate the molecular weight of X

Sol. The given values are

$$W_{\text{urea}} = 7 \text{ g}$$

$$W_{\rm v} = 42 {\rm g}$$

$$W_{\Delta} = 100 \text{ g}$$

Now using formula,
$$Mw_{\rm B} = \frac{K_{\rm f} \times W_{\rm B} \times 1000}{\Delta T_{\rm f} \times W_{\rm A}}$$

For urea,
$$Mw_{\rm B} = \frac{K_{\rm f} \times 7 \times 1000}{\Delta T_{\rm f} \times 100} = 60$$

For
$$X Mw'_{B} = \frac{K_{f} \times 42 \times 1000}{\Delta T_{f} \times 1000}$$
 ...(ii)

...(i)

Dividing Eq. (i) from Eq. (ii), we get

$$\frac{60}{Mw'_{\rm B}} = \frac{7}{42} \text{ or } Mw'_{\rm B} = 360$$

 \therefore Molecular weight of X = 360 g mol⁻¹

ILLUSTRATION 2.131

The freezing point of 0.02 mole fraction acetic acid in benzene is 277.4 K. Acetic acid exists partly as dimer. Calculate the equilibrium constant for dimerization. The freezing point of benzene is 278.4 K and the heat of fusion of benzene is 10.042 kJ mol⁻¹. Assume molarity and molality same.

Sol. For benzene, $K'_{\rm f} = \frac{RT^2}{1000l_{\rm f}({\rm cal}\ {\rm g}^{-1})}$

$$= \frac{8.314 \times (278.4)^2}{1000 \times \frac{10.042 \times 10^3}{70}} = 5.0 \text{ K molality}$$

Also,

For acetic acid in benzene

Before association After association $C(1-\alpha)$

$$\therefore K_{\rm C} = \frac{2}{C^2(1-\alpha)^2}$$

where α is the degree of association.

Also
$$\Delta T = K'_f \times \text{molality} \times \left(1 - \frac{\alpha}{2}\right)$$
 ...(ii)

 $\left(\because \text{ Total particles at equilibrium} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \right)$

Given mole fraction of acetic acid = $0.02 = \frac{n_2}{n_2 + n_1}$

 $\therefore \text{ Mole fraction of benzene} = 0.98 = \frac{n_1}{n_1 + n_2}$

$$\frac{n_2}{n_1} = \frac{0.02}{0.98}$$

.. Molality =
$$\frac{n_2}{W_1} \times 1000$$

= $\frac{n_2 \times 1000}{n_1 \times Mw_1} = \frac{0.02 \times 1000}{0.98 \times 78} = 0.262 \text{ m}$

$$\therefore \text{ From Eq. (ii), } 1 = 5 \times 0.262 \times \left(1 - \frac{\alpha}{2}\right)$$

$$\alpha = 0.48$$

From Eq. (i), assuming molarity = molality

$$K_{\rm C} = \frac{0.262 \times 0.48}{2 \times (0.262)^2 \times (1 - 0.48)^2} = 3.39$$

ILLUSTRATION 2.132

The freezing point of 0.08 molal NaHSO₄ is -0.345°C. Calculate the percentage of ${\rm HSO_4}^{\odot}$ ions that transfers a proton to water. Assume 100% ionization of NaHSO₄ and K_f for H₂O = 1.86 K molality⁻¹.

: Total particles after dissolution of NaHSO₄

$$= 1 + 1 - h + h + h = 2 + h$$

Now, $\Delta T_f = K_f \times \text{molality} \times (2 + h)$

$$0.345 = 1.86 \times 0.08 \times (2+h)$$

$$\therefore 2 + h = 2.319$$

$$h = 0.319$$

i.e., 31.9 % of ${\rm HSO_4}^{\odot}$ shows proton transfer to ${\rm H_2O}$.

ILLUSTRATION 2.133

Given that the latent heat of fusion of naphthalene is 19.0 kJ mol⁻¹ and its melting point is 80.2°C. Estimate the solubility of naphthalene in benzene at 76.2°C.

Sol. Given

$$T^{\circ} = 80.2^{\circ}\text{C}; T_{s} = 76.2^{\circ}\text{C}$$

$$\Delta_{\text{fus}}H = 90.0 \text{ kJ mol}^{-1}$$

For an ideal solution

$$\log \chi_2 = \frac{\Delta H}{2.303 R(T^{\circ})^2} (T_S - T^{\circ}) \qquad ...(i)$$

$$\Delta H = 19000 \text{ J}, T_s - T^\circ = -4^\circ \text{C},$$

$$R = 8.314$$

Substituting all values in Eq. (i),

$$\log \chi_2 = \frac{19000}{8.314 \times 2.303 \times (353.20)^2} \times (-4)$$

or
$$\chi_2 = 0.929 \approx 0.9$$

ILLUSTRATION 2.134

If a solution containing 6 g of triphenyl methane, (C₆H₅)₃CH (molecular weight = 244), in 1000 g of benzene is cooled to 0.22°C below the freezing point of benzene, how much solvent will crystallize out and what will be the molality of residual solution? $(K_f = 5.1 \text{ K m}^{-1})$

Sol. If the weight of benzene remaining as a liquid be W_1 g and assuming triphenyl methane to be soluble in liquid benzene, $\Delta T_{\rm f} = K_{\rm f} \times m$ $\Delta T_{\rm f} = 0.22$, $K_{\rm f} = 5.1~{\rm K~m}^{-1}$

assuming tripnenty methalic to be soluble in
$$\Delta T_c = K_c \times m$$
 $\Delta T_f = 0.22$, $K_f = 5.1 \text{ K m}^{-1}$

$$0.22 = 5.1 \times m$$

$$m = 0.0431372 = 0.043$$

$$m = \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

$$0.043 = \frac{6 \times 1000}{244 \times W_1} \implies W_1 = 571.86 \text{ g}$$

Amount of benzene crystallizing out

$$= 1000 - 571.16 = 428.14 g$$

ILLUSTRATION 2.135

A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm3 of benzene (density 0.889 g cm⁻³). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal the freezing point depression constant of

Sol. Using Raoult's law $P_1 = \chi_1 P_1^{\circ}$

We get (98.88 mm Hg) = χ_1 (100 mm Hg)

or
$$\chi_1 = 0.9888$$

Let 1 mol be the total amount of solvent and solute. We will

$$n_1 = 0.9888 \text{ mol}$$

$$n_2 = 0.0112 \text{ mol}$$

$$n_1 = 0.9888 \text{ mol}$$
 $m_2 = 0.9888 \text{ mol}$ $m_1 = n_1 M w_1 = (0.9888 \text{ mol}) (78 \text{ g mol}^{-1}) = 77.126 \text{ g}$

The molality of the solution is

$$m = \frac{n_1}{W_1} = \frac{0.0112 \text{ mol}}{77.126 \times 10^{-3} \text{ kg}} = 0.1452 \text{ mol kg}^{-1}$$

Molal freezing point depression constant of benzene would

$$K_{\rm f} = \frac{-\Delta T_{\rm f}}{m} = \frac{0.73 \text{ K}}{0.1452 \text{ mol kg}^{-1}} = 5.028 \text{ K kg mol}^{-1}$$

Questions based on when excess of solvent e.g., H2O is taken which separates out as ice on cooling

ILLUSTRATION 2.136

Calculate the amount of ice that will separate out on cooling containing 50 g of ethylene glycol in 200 g of water to -9.3°C. $(K_{\rm f} \text{ for water} = 1.86 \text{ K m}^{-1})$

Sol. Here mass of solute = 50 g

$$\Delta T_{\rm f} = 9.3^{\circ}$$
; $K_{\rm f} = 1.86 \text{ K m}^{-1} \text{ kg}$

Molecular mass of solute $(CH_2OH)_2$, $Mw_2 = 62$

We have to calculate the mass of water in which the given mass of solute will dissolve. The rest of water will freeze out as ice. Applying the relation

$$Mw_2 = \frac{1000 \cdot K_f \cdot W_2}{W_1 \cdot \Delta T_f}$$

$$W_1 = \frac{1000 \cdot K_f \cdot W_2}{M w_2 \cdot \Delta T_f} = \frac{1000 \times 1.86 \times 50}{62 \times 9.3} = 161.3 \text{ g}$$

Ice that will separate out = 200 - 161.3 = 38.7 g.

ILLUSTRATION 2.137

1000 g of 1 molal aqueous solution of sucrose is cooled and maintained at -3.534°C. Find out how much ice will separate out at this temperature. (K_f for water = 1.86 K m⁻¹.)

Sol. 342 g in 1000 g of $H_2O = 1 \text{ m}$

Weight of solution = 1342 g

1342 g contains =
$$1000 \text{ g of H}_2\text{O}$$

1000 g contains
$$\equiv \frac{1000}{1342} \times 1000 \equiv 745.156 \text{ g of H}_2\text{O}$$

Let x g of water remains in liquid state.

x g of H₂O dissolves in 1 mol solute.

745.15 g of H₂O dissolves =
$$\frac{1}{x} \times 745.156$$
 mol of solute $\Delta T_f = K_f \times m$

$$3.534 = 1.86 \times \frac{745.156}{x}$$
$$x = 392.18 \text{ g}$$

Amount of water separates as ice

$$= 745.156 - 392.18$$

$$= 352.98 g$$

Alternate method

$$1 \text{ m} = 342 \text{ g per } 1000 \text{ g of H}_2\text{O}$$

Find sugar in 1000 g of solution.

$$1342 \text{ g solution} \equiv 342 \text{ g sugar}$$

$$1000 \text{ g solution} = \frac{342 \times 1000}{1342}$$

= 254.85 g

Mass of
$$H_2O$$
 per 1000 g solution = 1000 - 254.85
= 745.15 g

$$\Delta T_{\rm f} = \frac{K_{\rm f} \times 1000 \times \text{grams of sucrose}}{Mw_{\rm sugar} \times \text{grams of H}_{\rm 2}\text{O left}}$$

$$= \frac{K_{\rm f} \times W_2 \times 1000}{Mw_2 \times W_1}$$

$$W_1 = \frac{K_{\rm f} \times W_2 \times 1000}{\Delta T_{\rm f} \times Mw_2}$$

$$= \frac{1.86 \times 254.84 \times 1000}{3.534 \times 342}$$

$$= 392.2 \text{ g H}_{\rm 2}\text{O}$$

Ice separates out =
$$745.15 - 392.2$$

= 352.95 g

Questions based on when excess of solute is taken which separates out on cooling

ILLUSTRATION 2.138

A 10 m solution of urea is cooled to -13.02°C. What amount of urea will separate out if the mass of solution taken is 100 g? $[K_f \text{ (water)} = 1.86 \text{ K m}^{-1}]$

Sol.
$$\Delta T_{\rm f} = 0 - (-13.02) = 13.02 \text{ K}$$

$$m = \Delta T_{\rm f}/K_{\rm f}$$

$$m = \frac{13.02}{1.86} = 7.0 \text{ mol kg}^{-1}$$

$$\therefore m = 10 = \frac{W_2 \times 1000}{60 \times (100 - W_2)}$$

$$\therefore W_2 = 37.5 \text{ g}$$

Mass of H_2O in this solution = (100 - 37.5) = 62.5 gThe mass of water does not change as urea separates out to

bring down the molality to 7 mol kg⁻¹.

$$\therefore m = \frac{W_2 \times 1000}{Mw_2 \times W_1}$$

$$\therefore 7 = \frac{W_2 \times 1000}{60 \times 62.5} \implies W_2 = 26.25 \text{ g}$$

Mass of urea separated = (37.5 - 26.25) = 11.25 g

The melting point of phenol is 40°C. A solution containing The metung relation (C₈H₉OH) in 12.54 g phenol freezes at 0.172 g Calculate the freezing point constant 0.172 g accumants the freezing point constant and the latent 39.25°C. Calculate the freezing point constant and the latent heat of fusion of phenol.

heat of fusion of phenom
heat of fusion of phenom

$$\Delta T_f = 40 - 39.25 = 0.75, Mw_2 = 135$$

$$K_f = \frac{\Delta T_f}{m} = \frac{0.75}{\frac{0.172}{135} \times \frac{1000}{12.54}} = 0.738 \text{ K kg m}^{-1}$$

$$= 7.38 \text{ per } 100 \text{ g}$$

$$T_f = 273 + 40 = 313 \text{ K}$$

$$T_{\rm f} = 273 + 40 = 313 \text{ K}$$

$$K_{\rm f} = \frac{RT_{\rm f}^2}{l \times 1000} = \frac{2 \times (313)^2}{l \times 1000}$$

$$l = \frac{2 \times (313)^2}{K_{\rm f} \times 1000} = \frac{2 \times (313)^2}{7.38 \times 1000} = 26.5 \text{ cal g}^{-1}$$

ILLUSTRATION 2.140

How much ethyl alcohol must be added to 1.00 L of water so that the solution will not freeze at -4°F?

Sol. Using relation

$$\Delta T_f = K_f m$$
where $\Delta T_f = -4^{\circ}F$
or $-4^{\circ}F = -20^{\circ}C$

$$\therefore m = \frac{\Delta T_f}{K_f} = \frac{20}{1.86} = 10.7$$

Therefore, amount of ethyl alcohol to be added

=
$$m \times \text{molecular weight}$$

= 10.7×46.0
= 495 g

2.10.4 OSMOSIS AND OSMOTIC PRESSURE

In nature we observe many phenomena, e.g., wilted flowers revive when placed in fresh water, blood cells get raptured when placed in brine (salt water). In all these natural phenomena we find one common, thing that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films. Yet they contain a network of submicroscopic holes or pores. Small solvent molecules, such as water, can pass through these holes but the passage of bigger molecules such as solutes is hindered. Membrane having this kind of properties are known as semi-permeable membranes. In laboratory these type of memberanes are not useful because of their imperfect nature. Consequently, they can be even artificially prepared. One such membrane is the film of gelatinous precipitate of cupric ferrocyanide, Cu₂[Fe(CN)₆].

Semi-permeable membranes: These are of two types:

a. Natural semi-permeable membranes: Membranes such as animal and vegetable membranes are found just under the

- outer skin of the animals and plants. The pig's bladder is the most common animal membrane used.
- b. Artificial semi-permeable membranes: Well-known examples of artificial semi-permeable membranes are parchment paper, cellophane, and certain freshly precipitated inorganic substances, e.g., copper ferrocyanide, silicates of iron, cobalt, nickel, silicates of iron, cobalt, nickel, copper ferrocyanide, etc. The precipitated substances have to be supported on some material and this is achieved by preparing the precipitate on the walls of a porous pot.

Osmosis

If we place a semi-permeable membrane between the solvent and solution as shown in Fig. 2.21 assuming that only solvent molecules can pass through these membrane, the solvent molecules will flow through the membrane from pure solvent side to the solution side. This flow of solvent from a region of higher concentration (i.e., pure solvent) to a region of lower concentration (i.e., solution) of solvent molecules is known as the phenomenon of osmosis. The phenomenon of osmosis was studied for the first time by Abbe Nollet in 1748.

As a result of osmosis, the level of solution in the tube rises, whereas that of the pure solvent falls. After some time an equilibrium is reached where the level of the solution in the tube does not rise further. At this stage, the excessive hydrostatic pressure created on the solution side exactly balances the tendency of the solvent to pass through the membrane as shown in Fig. 2.21(b). This excessive hydrostatic pressure is known as the osmotic pressure of the solution and is represented by symbol π . Thus, osmotic pressure may be defined as the excess pressure which must be applied to a solution to prevent the passage of solvent into it through a semi-permeable membrane.

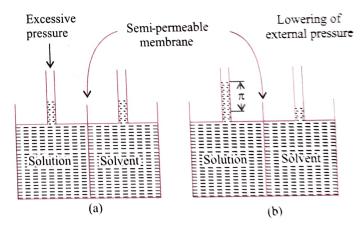


Fig. 2.21 Osmotic pressure of the solution

Osmosis can also take place between the solutions of different concentrations. In such cases, the solvent molecules move from the solution of low solute concentration to that of higher solute concentration.

The phenomenon of osmosis can be checked by increasing the external pressure on the solution by an amount equivalent to the hydrostatic pressure as shown in Fig. 2.21(b). Alternatively, this can also be checked by reducing the external pressure on the solvent side by an amount equivalent to the hydrostatic pressure.

Difference Between Osmosis and Diffusion

Diffusion and osmosis both involve the movement of the molecules, still they differ in the following respects:

Osmosis	Diffusion
a. The process of osmosis takes place through a semi-permeable	a. No semi-permeable membrane is needed for the diffusion process.
membrane. b. The osmosis involves the movement of the solvent molecules only.	b. In diffusion both the solute and solvent molecules can move.
c. In osmosis, molecules of solvent move from a region of lower conc- entration of solution into a region of higher	c. In diffusion, the molecules move from a region of higher concentration to a region of lower concentration.
d. Osmosis is limited to liquid solutions only.	d. Diffusion is common in gases as well as in liquids.
e. Osmosis can be stopped or reversed by applying additional pressure on the higher concentration side.	e. It cannot be stopped or reversed.

Osmotic Pressure: A Colligative Property

The osmotic pressure of a solution depends on its concentration larger the concentration larger the osmotic pressure.

Van't Hoff (1887) made a thorough study of the osmotic pressure of the dilute or ideal solution. He concluded that a dilute or ideal solution behaves like an ideal gas and the different gas laws are applicable to the dilute solution as well. Van't Hoff observed that for dilute solutions, the osmotic pressure (π) is proportional to the molarity, C of the solution at a given temperature T.

Thus,
$$\pi = CRT$$

Here π is the osmotic pressure and R is the gas constant. Equation (i) is known as the van't Hoff equation for osmotic pressure of the solution.

The determination of the molar mass of solute includes following steps:

According to the Van't Hoff equation,

$$\pi = CRT$$

But $C = \frac{n_{\rm B}}{V}$, where V is the volume of a solution in litres containing n_2 moles of solute.

$$\therefore \pi = \frac{n_{\rm B}}{V} RT \qquad ...(ii)$$

If $W_{\rm B}$ grams of solute of molar mass; $Mw_{\rm B}$ is present in the solution, then $n_{\rm B} = \frac{W_{\rm B}}{Mw_{\rm D}}$

$$\pi V = \frac{W_{\rm B}RT}{Mw_{\rm B}} \qquad ...(iii)$$

$$or Mw_{\rm B} = \frac{W_{\rm B}RT}{\pi V}$$

Thus, knowing the quantities W_2 , T, π , and V, we can calculate ψ_0 molar mass of the solute.

The principal application of osmotic pressure measurement The principal application of the molar mass of a substance which is in the determination of the molar mass of a substance which is either slightly soluble or has a very higher molar mass such as proteins, polymer of various types, and colloid. The osmolic pressure method has the advantage over other methods as pressure. measurement is around the room temperature and the molarly of solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilugative solutions. The technique of osmotic pressure for determination of molar mass of solute is particularly useful for biomolecules at they are generally not stable at higher temperature and polymer have poor solubility.

Osmotic pressure of mixture of two solutions

Case I: Let two solutions of same substance having different osmotic pressures π_1 and π_2 are mixed. The osmotic pressure of the resultant solution can be calculated as

$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

where V_1 and V_2 are the volumes of two solutions and $\pi_{\rm R}$ is the resultant osmotic pressure.

Case II: Let n_1 and n_2 are the number of moles of two different solutes present in V_1 and V_2 volumes, respectively.

The osmotic pressure of the mixture can be calculated as

$$\pi = \pi_1 + \pi_2 = \frac{n_1 i_1 RT}{(V_1 + V_2)} + \frac{n_2 i_2 RT}{(V_1 + V_2)}$$
$$\pi = \frac{(n_1 i_1 + n_2 i_2)}{(V_1 + V_2)} RT$$

Here i_1 and i_2 are Van't Hoff factor for the two solutes.

Isotonic, Hypertonic, and Hypotonic Solutions

When two solutions of different osmotic pressure are separated by semi-permeable membrane, the solvent molecules flow from the solutions of lower osmotic pressure towards the solution of higher osmotic pressure. This process continue till both the solution attain the same osmotic pressure. At this stage, there is no further osmosis. Such solutions having same osmotic pressure are called isotonic solutions or isomotic pressure.

From the equation, $\pi = CRT$, it is clear that if two solutions have same concentrations, they must have same osmotic pressur at same temperature. Thus, solutions of equimolar concentration at the same temperature have same osmotic pressure, i.e., and isotonic. If a solutions has more osmotic pressure than some other solution, it is called *hypertonic*. On the other hand a solution having less osmotic pressure than the other solution is called hypotonic solution. Thus, a hypertonic solution is more concentrated with respect to add with respect to other solution and a hypotonic solution is concentrated with respect to the other solution. For example, the osmotic process the osmotic pressure associated with the fluid inside the blood cell is equivalent to it. cell is equivalent to that of 0.9% (mass/volume) NaCl solution (i.e., isotopic) and in the solution of the sol (i.e., isotonic) called normal saline solution, and it is safe! inject intravenously. inject intravenously. On the other hand if we place the cells in

solution containing more than 0.9% NaCl, water will flow out of the cells and they would shrink (i.e., hypertonic solution). If the salt concentration is less than 0.9% (hypotonic solution), water will flow into the cells and they would swell.

Experimental method for determination of osmotic pressure

There are various methods employed experimentally to determine osmotic pressure, few of them are listed below:

- a. Pfeffer's method
- b. Morse and Frazer's method
- c. Berkeley and Hartley's method

From the above-listed methods, Berkeley and Hartley's method is widely used.

Biological Importance of Osmosis

The growth of plants and animals depends largely on the phenomenon of osmosis. Plant and animal bodies are composed of a very large number of microscopic units called *cells*. Cells contain a fluid and are composed of a living cytoplasmic membrane which behaves as semi-permeable membrane and is responsible for the phenomenon of osmosis in living organism.

When a cell comes in contact with water or some dilute solution, the osmotic pressure of which is less than that of cell fluid present into the cell, there becomes a tendency of water to enter into the cell through the cell wall. This causes rupturing of the cell, a process known as *hemolysis*. The pressure developed inside the cell due to the inflow of water into it is called *turgor*. On the other hand, if the cell comes in contact with a solution of higher osmotic pressure, the cell would shrink due to the water going out of the cell through the cell wall. This shrinking of the cell is called *plasmolysis* or *crenation*.

Following are some processes regulated by osmosis in plants and animals:

- a. Plants absorb water from the soil through their roots due to osmosis because the concentration of cell gap inside root hair cells is higher than that of the water present in the soil.
- **b.** Osmosis helps in the rapid growth of plants and in the germination of seeds.
- c. Bursting of red blood cells when placed in water is also due to osmosis.
- **d.** Different movements of plants such as opening and closing of flowers, etc., are controlled by osmosis.
- e. A 0.91% solution of pure NaCl is *isotonic* with human red blood cells (RBCs). Therefore, in this solution, RBCs neither swell nor undergo plasmolysis.
- f. A pure NaCl solution with concentration less than 0.91% is called *hypotonic solution*. On placing RBCs in this solution, they will swell and even burst.
- **g.** A pure NaCl solution with concentration more than 0.91% is called *hypertonic solution*. On placing RBCs in this solution, they shrink due to plasmolysis.
- h. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called *edema*.

i. The use of salt and sugar as preservatives in pickels and jams has its basis in preventing growth of fungi and bacteria by osmosis.

2.10.5 REVERSE OSMOSIS

The direction of osmosis can be reversed by applying higher pressure than the osmotic pressure to the solution side. As a result of this the solvent starts flowing from solution side towards the pure solvent through the semi-permeable membrane. Thus, reverse osmosis is the process of movement of solvent through semi-permeable membrane from the solution to the pure solvent by applying excess pressure on the solution side.

This phenomenon has got a great practical utility. Reverse osmosis is used in water purification and desalination of sea water. For this purpose a variety of polymers are available these days. The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water.

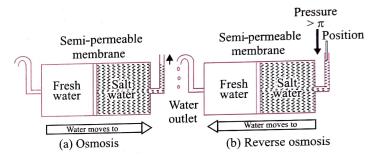


Fig. 2.22 A schematic set up for the reverse osmosis used for desalination of sea water

In Fig. 2.22(a), when there is no any external pressure applied to the salt water solution, fresh water flows towards salt water through semi-permeable membrane due to osmosis process. When a pressure greater than the osmotic pressure (π) is applied on the salt water [Fig. 2.22(b)], the pure water flows from the salt water side to pure water side through semi-permeable membrane. As a result water is squeezed out of sea water. Thus, pure water is obtained which does not contain any dissolved undesirable salt.

2.10.6 RELATIONSHIPS BETWEEN DIFFERENT COLLIGATIVE PROPERTIES

Osmotic Pressure (π) with Relative Lowering of Vapour Pressure

Osmotic pressure
$$(\pi) = CRT = \frac{n_2}{V}RT$$
 ...(i)

Relative lowering of vapour pressure

$$\Rightarrow \frac{P^{\circ} - P_{S}}{P^{\circ}} = \chi_{2} \approx \frac{n_{2}}{n_{1}}$$
or $n_{2} = n_{1} \times \left(\frac{P^{\circ} - P_{S}}{P^{\circ}}\right)$

$$= \frac{W_{1}}{Mw_{1}} \left(\frac{P^{\circ} - P_{S}}{P^{\circ}}\right) \qquad ...(ii)$$

Substituting Eq. (ii) in Eq. (i),

$$\pi = \frac{W_1 RT}{V M w_1} \left(\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} \right)$$

$$= \frac{dRT}{M w_1} \left[\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} \right] \qquad \left[d(\text{density}) = \frac{W_1}{V} \right]$$

Osmotic Pressure (π) with Elevation in Boiling Point (ΔT_b)

Elevation in boiling point $(\Delta T_b) = K_b m = \frac{K_b \times n_2 \times 1000}{W_1}$

or
$$n_2 = \frac{\Delta T_b \times W_1}{K_b \times 1000}$$
 ...(iii)

Substituting Eq. (iii) in Eq. (i),

$$\pi = \frac{\Delta T_b \times W_1 \times RT}{V \times K_b \times 1000}$$

$$= \frac{\Delta T_b RT}{K_1 \times 1000} \times \frac{W_1}{V} = \frac{\Delta T_b RT \times d}{K_b \times 1000}$$

$$\left[d = \frac{W_1}{V} \right]$$

Osmotic Pressure (π) with Depression in Freezing Point (ΔT_c)

Depression in freezing point $(\Delta T_f) = K_f m = \frac{K_f \times n_2 \times 1000}{W_1}$

$$orn_2 = \frac{\Delta T_f \times W_1}{K_f \times 1000} \qquad ...(iv)$$

Substituting Eq. (iv) in Eq. (i),

$$\pi = \frac{\Delta T_{\rm f} \times W_{\rm l} \times RT}{K_{\rm f} \times 1000 \times V}$$

$$= \frac{\Delta T_{\rm f} \times dRT}{K_{\rm f} \times 1000}$$

$$d = \frac{W_{\rm l}}{V}$$

Elevation in Boiling Point with Relative Lowering of Vapour Pressure

Elevation in boiling point $(\Delta T_b) = K_b m = \frac{K_b \times n_2 \times 1000}{W_1}$...(v)

Relative lowering of vapour pressure

$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \chi_{2} \approx \frac{n_{2}}{n_{1}} = \frac{n_{2}}{n_{1}} \times Mw_{1} \qquad \left[n_{1} = \frac{W_{1}}{Mw_{1}} \right]$$

$$\operatorname{or} n_2 = \left(\frac{P^{\circ} - P_{\mathsf{S}}}{P^{\circ}}\right) \times \frac{W_1}{Mw_1} \qquad \dots (vi)$$

Substituting Eq. (vi) in Eq. (v),

$$\therefore \Delta T_{\rm b} = \frac{1000 \times K_{\rm b}}{Mw_{\rm i}} \left(\frac{P^{\rm o} - P_{\rm S}}{P^{\rm o}} \right)$$

Depression in Freezing Point with Lowering of Vapour Pressure

Depression in freezing point $(\Delta T_f) = K_f m = \frac{K_f \times n_2 \times 1000}{W_1}$...(vii)

Lowering in vapour pressure

$$\frac{P^{\circ} - P_{S}}{P^{\circ}} = \chi_{2} \approx \frac{n_{2}}{n_{1}} = \frac{n_{2}}{W_{1}} \times Mw_{1} \qquad \left[n_{1} = \frac{W_{1}}{Mw_{1}} \right]$$

$$\therefore n_2 = \left(\frac{P^{\circ} - P_{\rm S}}{P^{\circ}}\right) \times \frac{W_1}{Mw_1}$$

Substituting Eq. (viii) in Eq. (vii),

$$\therefore \Delta T_{\rm f} = \frac{1000 \times K_{\rm f}}{M w_{\rm l}} \left(\frac{P^{\circ} - P_{\rm S}}{P^{\circ}} \right)$$

ILLUSTRATION 2.141

Define osmotic pressure.

Sol. Osmotic pressure is the extra pressure that is to be applied on the solution side when the solution and solvent are separated by a semi-permeable membrane to stop osmosis.

 $\cdot\cdot\cdot(v_{\hat{l}\hat{j}})$

ILLUSTRATION 2.142

What is reverse osmosis?

Sol. When the hydrostatic pressure applied on the solution side is more than the osmotic pressure of solution, then solven molecules from solution side enter in to the solvent side through semi-permeable membrane. This process is called reverse Osmosic

ILLUSTRATION 2.143

Briefly explain the underlying principle of the purification of water by reverse osmosis.

Sol. When pressure greater than osmotic pressure is applied the salt water side of a semi-permeable membrane, water molecular flow through the membrane towards pure water side.

ILLUSTRATION 2.144

State how does osmotic pressure vary with temperature?

Sol. Osmotic pressure increases with increase in temperature

ILLUSTRATION 2.145

What are isotonic solutions?

Sol. Two solutions which have the same osmotic pressure if called isotonic solutions.

ILLUSTRATION 2.146

Outer hard shells of two eggs are removed. One of the eggs be placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why?

pure water into the egg. On the other hand, the egg placed in the saturated solution of NaCl will shrink due to the osmosis of water out of the egg. This is because osmosis always occurs from higher concentration of solvent to lower concentration of solvent.

ILLUSTRATION 2.147

When dehydrated fruits and vegetables are placed in water, they slowly swell and return to original form. Why? Would temperature increase accelerate the process? Explain.

The cell walls of fruits and vegetables are semi-permeable. The liquid inside the cells in the dried fruits and vegetables is more concentrated. When these dried fruits and vegetables are placed in water, water enters the fruits and vegetables due to osmosis and they swell and return to their original form. Since the increase in temperature increases the osmotic pressure $(\pi \propto T)$, the process gets accelerated.

ILLUSTRATION 2.148

Why is great care taken in intravenous injections to have comparable concentration of solutions to be injected to that of blood plasma?

During intravenous injections, the concentrations of the solution to be injected should be comparable to blood plasma. If the solution is less concentrated, its osmotic pressure will be low. The water will try to move into the red blood cells through the cell walls. As a result, cells will swell and burst. On the other hand, if the solution is more concentrated, the water in the cells will try to move outside the cell to the more concentrated solution by osmosis. This causes cells to shrink and consequently cease to function.

ILLUSTRATION 2.149

be determined accurately.

Which colligative property is preferred for the molar mass determination of macromolecules (i.e., proteins and polymers)?

Sol.

a. The molecular weight of macromolecules (e.g., proteins and polymers) is very high, hence the measured values $\left(\text{e.g.}, \frac{\Delta P}{P^{\circ}}, \Delta T_{\text{f}}, \Delta T_{\text{b}}\right)$ will be very less and thus cannot

Although the osmotic pressure will also be less but it can be measured, since it is not the difference in pressure as in the cases of other colligative properties.

b. The osmotic pressure is measured at room temperature. So the properties of macromolecules do not change, whereas all other methods require heating which changes the properties of macromolecules, e.g., the proteins may coagulate and polymers may decompose at higher temperature.

ILLUSTRATION 2.150

Addition of HgI_2 to the aqueous solution of KI shows an increase in the osmotic pressure, why?

Sol. HgI₂ forms a complex with KI, and therefore, the number of particles in solution increases.

$$\mathrm{HgI}_2 + 2\mathrm{KI} \to \mathrm{K}_2[\mathrm{HgI}_4] \ensuremath{\ensuremath{\mathrm{Hg}}} 2\mathrm{K}^\oplus + [\mathrm{HgI}_4]^{2-}$$

Therefore, the osmotic pressure increases.

ILLUSTRATION 2.151

What will happen if pressure greater than the osmotic pressure is applied on the solution separated by a semi-permeable membrane from the solvent?

Sol. It will result into reverse osmosis, i.e., there will be net flow of the solvent from the solution to the solvent.

ILLUSTRATION 2.152

What is osmotic pressure and how is it related with the molecular mass of a non-volatile substance? What advantage the osmotic pressure method has over the elevation of boiling point method for determining molecular masses?

Sol. For definition of osmotic pressure, refer to Section 2.10.4.

$$\begin{split} \pi V &= nRT \\ \pi &= \frac{n}{V}RT = \frac{W_{\rm B} \times R \times T}{Mw_{\rm B} \times V} \\ Mw_{\rm B} &= \frac{W_{\rm B} \times R \times T}{\pi \times V}, \end{split}$$

where $Mw_{\rm R}$ is the molar mass of the solute.

The advantage of the osmotic pressure method is that it is measured at room temperature. It is convenient to measure at room temperature than at boiling point. The value of osmotic pressure is quite appreciable even for very dilute solutions of polymers as compared to that of elevation boiling point.

ILLUSTRATION 2.153

Why a person suffering from high blood pressure is advised to take minimum quantity of common salt?

Sol. The osmotic pressure is directly proportional to the concentration of solutes. Our body fluid contains a number of solutes. On taking large amount of common salt, Na[®] and Cl[®] ions enter into the body fluid thereby raising the concentration of the solutes. As a results, osmotic pressure is increased which may rapture the blood cells.

ILLUSTRATION 2.154

Blood freezes at 272.44 K and a solution of 3.0 g of urea in 250 g of water freezes at 272.63 K. Calculate the osmotic pressure of blood at 300 K. (Assume density of blood at 300 K to be 1 g cc^{-1})

Sol. In this question first calculate K_f of water from urea solution.

$$\Delta T_{\rm f} = K_{\rm f} \left(\frac{\frac{W_{\rm B}}{Mw_{\rm B}}}{W_{\rm A}} \times 1000 \right)$$

$$\Rightarrow K_{\rm f} = \frac{\Delta T_{\rm f}}{\left(\frac{W_{\rm B}}{Mw_{\rm B}} \times 1000 \right)}$$

$$\Rightarrow K = \frac{0.37}{1000}$$

$$\Rightarrow K_{\rm f} = \frac{0.37}{\left(\frac{3}{60} \times 1000\right)} = 1.85$$

$$[\Delta T_{\rm f} = 273 - 272.63 = 0.37 \text{ K}]$$

Now determine the molality of blood by using

$$\Delta T_{\rm f} = K_{\rm f} m$$

Now
$$\Delta T_{\rm f} = 273 - 272.44 = 0.56$$
°C

$$m = \frac{\Delta T_{\rm f}}{K_{\rm f}} = \frac{0.56}{1.85} = 0.303$$

Note: Colligative properties are defined for dilute solution. Assume molarity = molality.

$$\Rightarrow$$
 Molarity = molality = 0.303

Now using
$$\pi = CRT$$

$$\Rightarrow \pi = 0.303 \times 0.082 \times 300 = 7.46 \text{ atm}$$

ILLUSTRATION 2.155

x g of non-electrolytic compound (molar mass = 200) is dissolved in $1.0\,L$ of $0.05\,M$ NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at 27°C. Calculate the value of x. Assume complete dissociation of NaCl and ideal behaviour of this solution.

Sol.

a. For NaCl:
$$\pi = iCRT = 2 \times 0.05 \times 0.0821 \times 300$$

= 2.463

b. For unknown compound:

$$\pi = CRT = \frac{x}{200} \times 0.0821 \times 300 = 0.1231x$$
 atm

Total osmotic pressure $\pi = \pi_1 + \pi_2$

$$4.92 = 2.463 + 0.1231x$$

$$x = 19.959 \text{ g}$$

ILLUSTRATION 2.156

The osmotic pressure of a solution is 1.3 atm. The density of solution is 1.3 g cm⁻³. Calculate the osmotic pressure rise. $(1 \text{ atm} = 76 \text{ cm Hg}, d_{\text{Hg}} = 13.6 \text{ g cm}^{-3})$

Sol.
$$\pi = hdg$$

$$1.3 \times 76 \times 13.6 \times g = h \times 1.1 \times g$$

$$h = \frac{1.3 \times 76 \times 13.6}{1.3} \text{ cm}$$
$$= 1033.6 \text{ cm}$$

ILLUSTRATION 2.157

Two solutions of glucose have osmotic pressure 1.5 and 2.5 atm, respectively. 1 L of first solution is mixed with 2 L of second solution. The osmotic pressure of the resultant solution will be

Sol. d.
$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

 $1.5 \times 1 + 2.5 \times 2 = \pi_R \times 3$
 $\pi_R = \frac{6.5}{3} = 2.16 \text{ atm}$

ILLUSTRATION 2.158

18 g glucose and 6 g urea are dissolved in 1 L aqueous solution at 27°C. The osmotic pressure of the solution will be

Sol. b.
$$\pi V = (n_1 + n_2) RT$$

$$\pi V = \left(\frac{W_1}{Mw_1} + \frac{W_2}{Mw_2}\right) RT$$

$$\pi \times 1 = \left(\frac{18}{180} + \frac{6}{60}\right) \times 0.0821 \times 300$$

$$\pi = 4.926 \text{ atm}$$

ILLUSTRATION 2.159

The osmotic pressure of decimolar solution of urea at 27°C in **b.** 5 bar

Sol. a.
$$\pi = CRT$$

= 0.1 × 0.083 × 300
= 2.49 bar

ILLUSTRATION 2.160

The osmotic pressure of a solution at 0°C is 4 atm. What will be its osmotic pressure at 546 K under similar conditions?

Sol.
$$\mathbf{c} \cdot \frac{\pi_1}{\pi_2} = \frac{CRT_1}{CRT_2}$$

$$\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$$

$$\frac{4}{\pi_2} = \frac{273}{546}$$

$$\pi_2 = 8 \text{ atm}$$

ILLUSTRATION 2.161

3% solution of glucose is isotonic with 1% solution of not volatile non-electrolyte solute. The molecular mass of the solute would be

Sol. d.
$$\pi_{\text{glucose}} = \pi_{\text{solute}}$$

$$C_{\rm glucose} = C_{\rm solute}$$

$$\left(\frac{W_{\rm B} \times 1000}{Mw_{\rm B} \times V}\right)_{\rm plucose} = \left(\frac{W_{\rm B} \times 1000}{Mw_{\rm B} \times V}\right)_{\rm solute}$$

$$\left(\frac{3 \times 1000}{180 \times 100}\right)_{\text{glucose}} = \left(\frac{1 \times 1000}{Mw_{\text{B}} \times 100}\right)_{\text{solute}}$$

$$Mw_{\rm R}(\text{solute}) = 60$$

ILLUSTRATION 2.162

 $_{300 \text{ cm}^3}$ of an aqueous solution contains 1.26 g a polymer. The $_{0smotic}$ pressure of such solution at 300 K is found to be 1.26 \times 10⁻³ bar. Calculate the molar mass of the polymer.

Sol.
$$\pi V = \frac{W_{\rm B}}{M w_{\rm B}} RT$$

$$Mw_{\rm B} = \frac{W_{\rm B}}{V} \times \frac{RT}{\pi}$$
$$= \frac{1.26}{0.3} \times \frac{0.083 \times 300}{1.26 \times 10^{-3}}$$

$= 83000 \text{ g mol}^{-1}$

ILLUSTRATION 2.163

The solution containing 10 g of an organic compound per litre showed an osmotic pressure of 1.18 atm at 0° C. Calculate the molecular mass of the compound (R = 0.0821 litre atm per degree per mol)

Sol. Applying the equation

$$Mw = \frac{W}{PV} \cdot RT$$

Given,
$$W = 10$$
 g, $P = 1.18$ atm, $V = 1$ L, $R = 0.0821$ and $T = 273$ K.

$$Mw = \frac{10}{1.18 \times 1} \times 0.0821 \times 273 = 189.94$$

ILLUSTRATION 2.164

Calculate the osmotic pressure of 5% solution of cane sugar (sucrose) at 300 K.

Sol. M_W = Molecular mass of sucrose $(C_{12}H_{22}O_{11}) = 342$

$$W = 5 \text{ g}, V = 300 \text{ mL} = 0.3 \text{ L}$$

$$R = 0.082$$
, $T = 300$ K

Applying the equation
$$\pi V = \frac{W}{Mw} RT$$

$$\pi = \frac{5}{342} \times \frac{1}{0.3} \times 0.082 \times 300$$

$$= 1.198 atm$$

ILLUSTRATION 2.165

A solution is prepared by dissolving 1.08 g of human serum albumin, a protein obtained from blood plasma, in 50 cm³ of aqueous solution. The solution has an osmotic pressure of 5.85 mm Hg at 298 K.

- a. What is the molar mass of albumin?
- **b.** What is the height of water column placed in solution? $d_{(H_2O)} = 1 \text{ g cm}^{-3}$

Sol.

a. The molar mass of albumin can be calculated using the following relation

$$Mw_{\rm B} = \frac{W_{\rm B} \times RT}{\pi V} \qquad ...(i)$$

Given,
$$W_B = 1.08 \text{ g}$$
; $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$T = 298 \text{ K}, \ \pi = \frac{5.85}{760} \text{ atm}; \ V = \frac{50}{1000} = 0.05 \text{ L}$$

Substituting these values in Eq. (i), we get

$$Mw_{\rm B} = \frac{1.08 \times 0.0821 \times 298}{(5.85 / 760) \times 0.05} = 68655 \text{ g mol}^{-1}$$

b.
$$\pi = hdg$$

$$\frac{5.85}{760} \times 101325 = h \times 1 \times 10^{-3} \times 9.8 \quad [1 \text{ atm} = 101325 \text{ Pa}]$$

$$h = 7.958 \times 10^{-2} \text{ m} = 7.958 \text{ cm}$$

ILLUSTRATION 2.166

A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea if the molecular mass of cane sugar is 342.

Sol. Let the molecular mass of urea be Mw_2 .

Molar concentration of sugar =
$$\frac{W_1}{Mw_1 \times V_1} = \frac{5}{342 \times 0.1}$$

Molar concentration of urea =
$$\frac{W_2}{Mw_2 \times V_2} = \frac{0.877}{Mw_2 \times 0.1}$$

For isotonic solution,

$$\frac{W_1}{Mw_1V_1} = \frac{W_2}{Mw_2V_2}$$

$$\frac{5}{342 \times 0.1} = \frac{0.877}{Mw_2 \times 0.1}$$

$$Mw_2 = \frac{0.877 \times 342}{5}$$
$$= 59.987$$

ILLUSTRATION 2.167

 $200~\rm cm^3$ of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.

Sol. The given values are

$$\pi = 2.57 \times 10^{-3} \text{ bar}$$

$$V = 200 \text{ cm}^3 = 0.2 \text{ L}$$

$$T = 300 \text{ K}$$

$$R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

$$Mw_{\text{solute}} = \frac{W_{\text{solute}} \times R \times T}{\pi \times V}$$

$$= \frac{1.26 \text{ g} \times 0.083 \text{ L bar mol}^{-1} \text{K}^{-1} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{bar} \times 0.2 \text{ L}}$$

$= 61022 \text{ g mol}^{-1}$

Thus, the molecular weight of solute is 61022 g mol⁻¹.

ILLUSTRATION 2.168

At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

Sol. The given values are

$$T = 300 \text{ K}$$

$$W_{\text{solute}} = 36 \text{ g}$$

$$\pi_1 = 4.98 \text{ bar}$$

$$\pi_2 = 1.52 \text{ bar}$$

$$V_{\text{solution}} = 1 \text{ L}$$

According to Van't Hoff equation,

$$\pi = CRT$$

$$C_1 = \frac{36}{180} \,\mathrm{M}, \quad C_2 = ?$$

$$\therefore$$
 4.98 bar = $\frac{36}{180}$ RT ...(i)

1.52 bar =
$$C_2 RT$$
 ...(ii),

Dividing Eq. (ii) by Eq. (i),

$$\frac{C_2}{36} \times 180 = \frac{1.52}{4.98}$$

$$\therefore C_2 = \frac{1.52}{4.98} \times \frac{36}{180} = 0.061 \,\mathrm{M}$$

Thus, the concentration of second solution is 0.061 M.

ILLUSTRATION 2.169

The osmotic pressure of blood is 8.21 atm at 310 K. How much glucose should be used per L for an intravenous injection that is isotopic with blood?

Sol. The given values are

$$\pi_{\text{(blood)}} = 8.21 \text{ atm}; V = 1 \text{ L}; T = 310 \text{ K}$$

$$\pi_{\text{(glucose)}} = 8.21 \text{ atm}$$
 (blood and glucose are isotonic)

(glucose) (exoduction grades are isotomic

Now, $\pi V = nRT$

or
$$n = \frac{\pi V}{RT}$$

$$\therefore n = \frac{8.21 \times 1.0}{0.0821 \times 300} = \frac{10}{31}$$

 \therefore Weight of glucose = $n \times$ Molecular weight

$$=\frac{10}{31}\times180=58.06 \text{ g}$$

ILLUSTRATION 2.170

A solution was prepared by dissolving 6.0 g an organic compound in 100 g of water. Calculate the osmotic pressure of this solution at 298 K, when the boiling point of the Solution is 100.2° C. (K_b for water = 0.52 K m⁻¹, R = 0.082 L atm K⁻¹ mol⁻¹)

Sol. The given values are

$$W_{\text{solute}} = 6.0 \text{ g}; W_{\text{solvent}} = 100 \text{ g}, K_{\text{b}} = 0.52 \text{ K m}^{-1}$$

 $\Delta T_{\text{b}} = 100.2 - 100 = 0.2$

Now using the formula

$$Mw_{\text{solute}} = \frac{K_{\text{b}} \times W_{\text{solute}} \times 1000}{\Delta T_{\text{b}} \times W_{\text{solvent}}}$$
$$= \frac{0.52 \times 6.0 \times 1000}{0.2 \times 100}$$

$$= 156 \text{ g mol}^{-1}$$

Now,
$$\pi = \frac{nRT}{V}$$
; $n = \frac{W_{\text{solute}}}{Mw_{\text{solute}}}$

$$\therefore n = \frac{6.0}{156}$$

$$\therefore \pi = \frac{6.0 \times 0.082 \times 298}{156 \times 0.1}$$

$$= 9.398 atm$$

Thus, the osmotic pressure of the solution is 9.398 atm

ILLUSTRATION 2.171

A solution obtained by mixing 100 mL of 20% solution of uniform (molar mass = 60) and 100 mL of 1.6% solution of cane sum (molar mass = 342) at 300 K. (R = 0.083 L bar K⁻¹ mol Calculate

- a. Osmotic pressure of urea solution
- b. Osmotic pressure of cane sugar solution
- c. Total osmotic pressure of solution

Sol. The given values are

$$W_{\text{urea}} = 2.0 \text{ g}; V = 200 \text{ mL}, T = 293 \text{ K}$$

 $W_{\text{cane sugar}} = 1.2 \text{ g}; Mw_{\text{urea}} = 60, Mw_{\text{cane sugar}} = 342$
 $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$

Now using Van't Hoff equation,

$$\pi = CRT \text{ or } \frac{W_2RT}{Mw_2V}$$

a. Osmotic pressure of urea

$$\pi = \frac{2.0 \times 0.083 \times 300}{60 \times 0.2} = 4.15 \, \text{bar}$$

b. Osmotic pressure of cane sugar

$$\pi = \frac{1.2 \times 0.083 \times 300}{342 \times 0.2} = 0.43 \text{ bar}$$

c. The total osmotic pressure of solution will be the sufficiency the osmotic pressure produced by urea and cane supplement respectively.

$$\therefore \pi_{\text{total}} = \pi_{\text{urea}} + \pi_{\text{cane sugar}}$$
$$= 4.15 + 0.43 = 4.58 \text{ bar}$$

ILLUSTRATION 2.172

The osmotic pressure of a solution containing 5 g of substance (molar mass = 100) in 308 mL of solution was found to be 4.0 atm at 300 K. Calculate the value of solution constant (R).

Sol. The given values are

$$W_{\rm B} = 5 \text{ g}; \quad Mw_{\rm B} = 100 \text{ g mol}^{-1}$$

 $\pi = 4.0 \text{ atm}; \quad T = 300 \text{ K}; \quad V = 308 \text{ mL}$

$$R = \frac{\pi V}{nT}$$

$$= \frac{4.0 \times \frac{308}{1000}}{\frac{5}{100} \times 300} = 0.0821 \text{ L-atm mol}^{-1} \text{ degree}^{-1}$$

ILLUSTRATION 2.173

The osmotic pressure of a solution was found to be 8 atm when 8 mol of a non-volatile solute was dissolved in VL of solution at 300 K. Calculate the volume of solution (R = 0.0821 L-atm K^{-1} mol⁻¹)

Sol. The given values are

$$\pi = 8 \text{ atm}; T = 300 \text{ K}; n_B = 8$$

$$R = 0.0821 \text{ L-atm mol}^{-1}$$

$$V = \frac{nRT}{\pi} = \frac{8 \times 0.0821 \times 300}{8} = 246.3 \text{ L}$$

ILLUSTRATION 2.174

Asolution of an organic compound is prepared by dissolving 30 gin 100 g water. Calculate the molecular mass of compound and the osmotic pressure of solution at 300 K, when the elevation in boiling point is 0.52 and $K_{\rm h}$ for water is 0.52 K m⁻¹.

Sol. The given values are

$$W_{\rm B} = 30 \text{ g}; W_{\rm A} = 100 \text{ g}; T = 300 \text{ K}$$

 $\Delta T_{\rm b} = 0.52; K_{\rm b} = 0.52 \text{ K m}^{-1}$

Now, using formula

$$Mw_{\rm B} = \frac{K_{\rm f} \times 1000 \times W_{\rm B}}{W_{\rm A} \times \Delta T_{\rm b}}$$

= $\frac{0.52 \times 1000 \times 30}{100 \times 0.52} = 300 \text{ g}$

For osmotic pressure,

$$\pi = \frac{nRT}{V} = \frac{W_{\rm B}}{Mw_{\rm B}} \times \frac{R \times T}{V} = \frac{30}{300} \times \frac{0.082 \times 300}{100/1000}$$
$$= 2.46 \text{ atm}$$

ILLUSTRATION 2.175

sum of

What will be the osmotic pressure of 0.1 M monobasic acid its pH is 2 at 25°C?

Sol.
$$HA \rightleftharpoons H^{\oplus} + A^{\odot}$$

 $[H^{\oplus}] = C\alpha = 10^{-2} \text{ M}$

$$\alpha = \frac{10^{-2}}{0.1} = 10^{-1} = 0.1$$

 \therefore Total particles in solution = 1 + α = 1 + 0.1 = 1.1

Now,
$$\pi = CRT(1 + \alpha)$$

= 0.1 × 0.0821 × 298 × 1.1
= 2.69 atm

ILLUSTRATION 2.176

 $100 \, \mathrm{mL}$ of $1.0 \, \mathrm{g}$ sample of a drug having compound $\mathrm{C_{21}H_{23}O_5N}$ as drug is coated with sugar lactose (mol. wt. 342) exerts the osmotic pressure of 0.70 atm at 27°C. What is the drug percentage in sample?

Sol. Let a, b g are the amount of drug (Mw = 369) and sugar (Mw = 342), respectively

$$a + b = 1.0 \dots (i)$$

$$\therefore \pi V = (n_1 + n_2) RT$$

$$0.70 \times \frac{100}{1000} = \left[\frac{a}{369} + \frac{b}{342} \right] \times 0.0821 \times 300$$
$$342a + 369b = 358.66 \qquad \dots(ii)$$

By Eqs. (i) and (ii)

$$a = 0.617 \text{ g}$$

$$b = 0.383 \text{ g}$$

$$\therefore$$
 % of drug = $\frac{0.617}{1} \times 100 = 61.7\%$

ILLUSTRATION 2.177

At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine the extent of dilution.

Sol. For initial solution, $\pi = \frac{500}{760}$ atm, T = 283 K

Using $\pi V = nRT$

$$\Rightarrow \frac{500}{760} \times V_1 = n \times R \times 283 \qquad \dots (i)$$

After dilution, let volume becomes V_2 and temperature is raised to 25°C, i.e., 298 K.

$$\pi = \frac{105.3}{760}$$
 atm

$$\frac{105.3}{760} \times V_2 = n \times R \times 298 \qquad ...(ii)$$

.. By Eqs. (i) and (ii), we get

$$\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500}$$

$$\frac{V_1}{V_2} = \frac{1}{5}$$

$$\Rightarrow V_2 = 5V_1$$

i.e., the solution was diluted to 5 times.

CONCEPT APPLICATION EXERCISE 2.2

- 1. The vapour pressure of ethyl alcohol at 25°C is 59.2 torr. The vapour pressure of a solution of non-volatile solute urea NH₂CONH₂ in ethyl alcohol is 51.3 torr. What is the molality of solution?
- 2. 30 mL of methyl alcohol (density = 0.8 g cm⁻³) is mixed with 70 mL of water (density = 1.0 g cm⁻³) at 25°C to give a solution of density 0.94 g cm⁻³. Find the mole fraction, molarity, and molality.
- 3. In winter, the normal temperature in a Himalayan's valley was found to be -10° C. Is a 30% by mass of aqueous solution of ethylene glycol (molar mass = 62) suitable for car radiator? (K_f for water = 1.86 K m⁻¹)
- 4. The vapour pressure of a very dilute aqueous solution and pure water is 17 and 17.39 mm at 20°C, respectively. Calculate the osmotic pressure at 20°C and density of water vapour at 20°C.

ANSWERS

- 1. m = 3.33
- **2.** $\chi_B = 0.16$; $\chi_A = 0.84$; Molarity = 7.5; molality = 10.58
- 3. -12.86 4. $\pi = 30.66$ atm; $d_{\text{H}_2\text{O}} = 1.673 \times 10^{-5} \text{ g mol}^{-1}$

2.11 ABNORMAL MOLAR MASSES: ELECTROLYTIC SOLUTIONS

Experiments on colligative properties of a solution reveals trustworthy results only if the following conditions are satisfied:

a. The solution must not be too concentrated

If the solution is concentrated, the particle begins to interact with each other as much as with the solvent. This obviously means that the vapour pressure starts to depend on the nature of the solute, and not just on the number of solute particles. Hence, to get the accurate values of molar mass the solution should be very dilute.

b. The solute must not undergo dissociation or association in the solution

As we know that colligative properties depend only upon the number of particles present in the solution irrespective to their nature, if the solute particle undergoes dissociation or association, the number of particles in solution changes and as a result of this the colligative properties also change. This result of discrepancy in the determination of molar mass of solute is called *abnormal molar mass*.

Let us discuss abnormal molar masses due to association or dissociation of solute particles. These two changes are being discussed below:

a. Association of solute particles

In a solvent of low dielectric constant or being non-polar, the solute molecules undergo association, i.e., two, three, or more molecules exist in combination with each other to form bigger molecules. For example, molecules of ethanoic acid (acetic acid) dimerize in benzene due to hydrogen bonding as shown below.

$$CH_3$$
 $-C$ O $-H$ $-O$ C $-CH_3$

Ethanoic acid dimer

Therefore, the total number of molecules in solution becomes less than the number of molecules of the substance added and therefore, colligative properties will be lower

Since the colligative properties are inversely proportional to the molar mass of the solute, the molar masses will be greater than the theoretical values. Then, ΔT_b or ΔT_f for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this ΔT_b or ΔT_f will, therefore be twice the expected value.

b. Dissociation of solute molecules

Let us suppose a solute gets dissociated or ionize in a solvent to give two or more particles. For example, a solute All dissociates to give cation and anion as:

$$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$$

Consequently, the total number of particles becomes twice in the solution and hence the colligative properties of such particles will be large and as the result of this the molar mass will be half the theoretical value.

For example, if we dissolve one mole of NaCl (58.5 g) in water, we expect one mole of each of K^{\oplus} and Cl^{\ominus} ions in be released in the solution. If this happens, there would be two moles of particles in the solution. Consequently, the colligative properties would also be about double than the expected. If we ignore interionic attraction, 1 mol of NaCl in 1 kg of water would be expected to increase the boiling point by 2×0.52 K ($K_b = 0.52$ K m⁻¹) = 1.04 K. Obviously the molar mass of the salt must be about half of its normal value, i.e., 37.5 g.

2.12 VAN'T HOFF FACTOR

When molecules in a solution undergo association and dissociation the colligative property for such solution is different from the ideal solution. This change in the property was explained by Van't Hoff In 1880, Van't Hoff introduced a factor *i*, known as the Van't Hoff factor, to account for the extent of dissociation or association. This factor *i* is defined as

 $i = \frac{\text{Normal (calculated) molecular mass}}{\text{Abnomal (observed) molecular mass}}$

$$= \frac{Mw_{\text{(calculated)}}}{Mw_{\text{(observed)}}} \text{ or } \frac{Mw_{\text{c}}}{Mw_{\text{o}}}$$

or

Total number of moles of particles after dissocation/assication

Number of moles of particles before dissociation/association

In case of association, observed molar mass being more than the normal, the factor *i* has value less than 1. But in case of dissociation, the Van't Hoff factor is more than 1 because the observed molar mass has a lesser value.

In case of solute which does not undergo any association or dissociation in a solvent, the Van't Hoff factor i will be equal to 1 because the observed and normal molar masses will be same.

Since the molar masses are inversely proportional to the colligative property, the Van't Hoff factor may also be expressed as:

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated colligative property}}$$

$$= \frac{P_{\text{obs}}}{P_{\text{calculated}}} = \frac{(\Delta P)_{\text{obs}}}{(\Delta P)_{\text{calculated}}}$$

$$= \frac{(\Delta T_{\rm b})_{\rm obs}}{(\Delta T_{\rm b})_{\rm calculated}} = \frac{(\Delta T_{\rm f})_{\rm obs}}{(\Delta T_{\rm f})_{\rm calculated}}$$

 $= \frac{\text{Actual number of particles in solution}}{\text{Number of particles taken}}$

Here, the calculated colligative properties are obtained by assuming that the non-volatile solute is neither associated or dissociated.

For example, the value of i for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Table 2.5 depicts values of the factor i for several strong electrolytes. For KCl, NaCl, and MgSO₄, Van't Hoff factor (i) approaches the value 2 as the solution becomes very dilute. As expected, the value of i gets close to 3 for K₂SO₄. Table 2.6 illustrates the Van't Hoff factor (i) for different solutes.

Table 2.5 Values of Van't Hoff factor (i) at various concentrations for NaCl, KCl, MgSO₄, and K_2SO_4

		i for complete		
Salt	0.1 m	0.01 m	0.001 m	dissociation
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
MgSO ₄	1.21	1.53	1.82	2.00
K ₂ SO ₄	2.32	2.70	2.84	3.00

Table 2.6 Van't Hoff factor (i) for different solutes

S. No.	Solute type	Example	lonization or association	Number of particles in the solution from 1 mol solute	Van't Hoff factor, i	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose		1	1	$Mw_{ m normal}$
2.	Binary electrolyte AB type	NaCl, KCl CH ₃ COOH	$\underset{1-\alpha}{AB} \Longleftrightarrow \underset{\alpha}{A}^{\oplus} + \underset{\alpha}{B}^{\ominus}$	2	1 + α	$\frac{Mw_{\text{normal}}}{1+\alpha}$
3.	Ternary electrolyte	$CaCl_2$, $BaCl_2$ H_2SO_4 , K_2 [PtCl ₆]	$AB_2 \rightleftharpoons A^{2+} + 2B^{\odot}$ $1 - \alpha = A^{2+} + 2B^{\odot}$	3	$1+2\alpha$	$\frac{Mw_{\text{normal}}}{1+2\alpha}$
	$(AB_2 \text{ type}$ or $A_2B \text{ type})$	112504, 112[1 1016]	$A_{2}B \rightleftharpoons 2A^{\oplus} + B^{2-}_{\alpha}$ $1-\alpha$	3	1 + 2a	$\frac{Mw_{\text{normal}}}{1+2\alpha}$
4.	Quaternary electrolyte	AlCl ₃ , K ₃ [Fe(CN) ₃]	$AB_3 \rightleftharpoons A_{\alpha}^{3+} + 3B_{\alpha}^{\odot}$ $1 - \alpha$	4	$1+3\alpha$	$\frac{Mw_{\text{normal}}}{1+3\alpha}$
	$(AB_3 \text{ or } A_3B \text{ type})$	FeCl ₃ , K ₃ PO ₄	$A_3 B \rightleftharpoons 3A^{\oplus} + B^{3-}_{\alpha}$ $1-\alpha \rightleftharpoons 3A^{\oplus} + B^{3-}_{\alpha}$	4	1+3d	$\frac{Mw_{\text{normal}}}{1+3\alpha}$
5.	Association of solute	Benzoic acid forming dimer in	$ \begin{array}{c} nA & \longrightarrow & An \\ & \alpha \\ & n \end{array} $	$\frac{1}{n}$	$\left[1-\left(1-\frac{1}{n}\right)\alpha\right]$	$\frac{Mw_{\text{normal}}}{\left[1-\left(1-\frac{1}{n}\right)\alpha\right]}$
6.	General electrolyte AB_{n-1}	benzene One mole of solute giving n ions in the solution	$AB_{n-1} \rightleftharpoons 1-\alpha$ $An^{+(n-1)} + (n-1)B^{\odot}$ $\alpha \qquad (n-1)\alpha$	n	$[1+(n-1)\alpha]$	$\frac{Mw_{\text{normal}}}{\left[1+(n-1)\alpha\right]}$

Inclusion of Van't Hoff factor modifies the equation for colligative properties as follows:

Relative lowering of the vapour pressure of solvent,

$$\frac{P_1^{\circ} - P_1}{P_1^{\circ}} = i \cdot \frac{n_2}{n_1} \text{ or } i\chi_2$$

Elevation of boiling point, $\Delta T_b = iK_b m$ Depression in freezing point, $\Delta T_f = iK_f m$ Osmotic pressure of solution, $\pi = iCRT$

2.12.1 CALCULATION OF THE EXTENT OF DISSOCIATION OR ASSOCIATION IN AN **ELECTROLYTIC SOLUTION**

The Van't Hoff factor may be used to calculate the extent of dissociation or association in terms of the degree of dissociation or association of a substance in a solution.

Degree of Dissociation

It is defined as the fraction of total substance that undergoes dissociation into ions.

Degree of dissociation =
$$\frac{\text{Number of moles of the substance dissociated}}{\text{Total number of moles}}$$
of the substance taken

Suppose a molecule of an electrolyte gives n ions after dissociation and α is the degree of dissociation, then at equiliburium

Number of moles of solute left undissociated = $1 - \alpha$ Number of moles of ions formed = $n\alpha$ Total number of moles of particles = $1 - \alpha + n\alpha$:. Van't Hoff factor,

$$i = \frac{\text{Observed number of moles of solute}}{\text{Normal number of moles of solute}} \text{ or}$$
Total number of moles at equilibrium

$$= \frac{Total\ number\ of\ moles\ at\ equilibrium}{Initial\ number\ of\ moles}$$

$$= \frac{1 - \alpha + n\alpha}{1}$$

$$\alpha = \frac{i - 1}{n - 1}$$

But
$$i = \frac{\text{Normal (calculated) molar mass}}{\text{Observed molar mass}} = \frac{Mw_{\text{(calculated)}}}{Mw_{\text{(observed)}}}$$

or
$$i = \frac{Mw_c}{Mw_o}$$

 $\therefore \alpha = \frac{Mw_c - Mw_o}{Mw_o (n-1)}$

Thus, knowing the value of observed molar mass and n, the degree of dissociation, α can be calculated.

Alternative method for the calculation of Van't Hoff factor in dissociation

Let α is the degree of dissociation.

.
$$i = (\text{number of ions after association} \times \alpha) + (1 - \alpha)$$

For example, let consider 50% ionization of
$$K_4[Fe(CN)_6]$$
 $K_4[Fe(CN)_6]$ $\longrightarrow 4K^{\oplus} + [Fe(CN)_6]^{4}$.

Initial moles 1 0 0

Final moles $1-\alpha$ 4α α

Total number of moles of equilibrium = $1-\alpha+4\alpha+\alpha$

$$i = \frac{\text{Total number of moles at equilibrium}}{\text{Initial moles}} = \frac{1+4\alpha}{1}$$

$$= 1+4\times0.5 = 1+2=3$$

Alternate method

i = [Number of ions after ionization
$$\times \alpha$$
] + $(1 - \alpha)$
= $(5 \times 0.5) + (1 - 0.5)$
= $2.5 + 0.5 = 3$

Degree of Association

It is defined as the fraction of total number of molecules which combine to form associated molecules.

Degree of association =
$$\frac{\text{Number of moles of the}}{\text{Total number of moles}}$$
of the substance taken

Suppose n molecules of the solute associate to form the associated molecule An and α is degree of association, then

$$nA = An$$

The concentration of species at equilibrium are:
Number of moles of solute left unassociated = $1 - \alpha$

Number of moles of solute after association = α/n Total number of moles after association = $1 - \alpha + \alpha / n$

$$\therefore \quad \text{Van't Hoff factor } (i) = \frac{\text{Observed number of}}{\text{Normal number of}} \text{ o}$$

$$\text{moles of solute}$$

= Total number of moles at equilibrium Initial number of moles

$$=\frac{1-\alpha+(\alpha/n)}{1}$$

$$i=1+\alpha(1/n-1)$$

or
$$\alpha = -\frac{i-1}{(1/n)-1}$$

Also,
$$i = -\frac{\text{Normal (calculate) molar mass}}{\text{Observed molar mass}} = \frac{Mw_c}{Mw_o}$$

$$\therefore 1 - \alpha + \frac{\alpha}{n} = \frac{Mw_c}{Mw_o}$$

or
$$1 - \frac{Mw_c}{Mw_o} = \alpha - \frac{\alpha}{n}$$

or
$$\frac{Mw_0 - Mw_c}{Mw_0} = \alpha \left(1 - \frac{1}{n}\right) = \alpha \left(\frac{n-1}{n}\right)$$

$$\therefore \quad \alpha = \frac{Mw_{\rm o} - Mw_{\rm c}}{Mw_{\rm c}} \left(\frac{n}{n-1}\right)$$

Thus, knowing n, the number of simple molecules which combine Thus, resident combine associated molecules, and observed molar mass, the degree to give associated molecules and observed molar mass, the degree $_{of association}(\alpha)$ can be calculated.

Alternative method for the calculation of Van't Hoff factor (i) in association

Let consider 60% association of CH₃COOH in benzene.

$$2(CH_3COOH) \longrightarrow (CH_3COOH)_2$$
1 moles 0

$$\begin{array}{ccc}
\text{CONSIDER Final moles} & 1 & & \frac{\alpha}{2} \\
\text{COOH}_{3} & & & \frac{\alpha}{2}
\end{array}$$

$$\begin{array}{cccc}
\text{CH}_{3} & & & \frac{\alpha}{2} \\
\text{CH}_{3} & & & \frac{\alpha}{2}$$

Total number of moles of equilibrium =
$$1 - \alpha + \frac{\alpha}{2}$$

$$i = \frac{\text{Total moles at equilibrium}}{\text{Intial moles}} = \frac{1 - \frac{\alpha}{2}}{1}$$

$$i = \frac{\text{Total moles at equilibrium}}{\text{Intial moles}} = \frac{1 - \frac{\alpha}{2}}{1}$$

$$0 = 1 - \frac{0.6}{2} = 1 - 0.3 = 0.7$$

$$\begin{bmatrix} 60\% \text{ association} \\ \text{i.e., } \alpha = 0.6 \end{bmatrix}$$

Alternate method

Let α is the degree of association.

$$i = \text{(Number of ions after association} \times \alpha) + (1 - \alpha)$$

= $\left(\frac{1}{2} \times 0.6\right) + (1 - 0.6)$

$$=0.3+0.4=0.7$$

Since i < 1, hence it represents association.

ILLUSTRATION 2.178

An M/10 solution of potassium ferrocyanide is 46% dissociated at 300 K. What will be its osmotic pressure?

Sol. Normal osmotic pressure =
$$\frac{W}{Mw \times V} \times R \times T$$

(When no dissociation has taken place) $\frac{W}{Mw}$ = 0.1, V = 1 L, R = 0.821, T = 300 K

Normal osmotic pressure =
$$\frac{0.1}{1} \times 0.0821 \times 300$$

= 2.463 atm

Potassium ferrocyanide is an electrolyte. It dissociates as

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^{\oplus} + [Fe(CN)_6]^4$$
 $(1-\alpha) \qquad 4\alpha \qquad \alpha$

Total number of particles =
$$1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$$

$$\alpha = 0.46$$
; so $1 + 4\alpha = 1 + 4 \times 0.46 = 2.84$

$$\frac{\text{Observed osomotic pressure}}{\text{Normal osomotic pressure}} = \frac{2.84}{1}$$

Observed osmotic pressure =
$$2.84 \times 2.463 = 6.995$$

ILLUSTRATION 2.179

A 0.5% aqueous solution of KCl was found to freeze at -0.24°C. Calculate the Van't Hoff factor and degree of dissociation of the solute at this concentration. (K_f for water = 1.86 K kg mol⁻¹)

Sol.
$$\Delta T_{\rm f} = i \times k_{\rm f} \times \frac{w_2 \times 1000}{Mw_2 \times W_1}$$

 $0.24 = i \times 1.86 \times \frac{0.5 \times 1000}{74.5 \times 99.5} \implies i = 1.92$

KCl
$$\rightleftharpoons$$
 K ^{\oplus} + Cl ^{\ominus} (α is the degree of ionization)
(1- α) α α
Total number of particles = 1 - α + α + α = 1 + α
 $i = 1 + \alpha$
1.92 = 1 + α
So, α = 1.92 - 1 = 0.92
i.e., 92% dissociated.

ILLUSTRATION 2.180

Two grams of benzoic acid (C₆H₅COOH) dissolved in 25.0 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg⁻¹ mol⁻¹. What is the percentage association of acid if it forms dimer in solution?

Sol.
$$W_2 = 2.0 \text{ g}, W_1 = 25.0 \text{ g}, \Delta T_f = 1.62 \text{ K},$$

 $K_f = 4.9 \text{ K kg}^{-1} \text{ mol}^{-1}, Mw_2(\text{C}_6\text{H}_5\text{COOH}) = 122 \text{ g mol}^{-1}$
Substituting these values in equation $\Delta T_f = i \times K_f \times m$

$$= i \times K_{f} \times \frac{W_{2} \times 1000}{Mw_{2} \times W_{1}}$$

1.62 K =
$$i \times 4.9$$
 K kg⁻¹ mol⁻¹ × $\frac{2.0 \text{ g} \times 1000}{122 \text{ g mol}^{-1} \times 25.0 \text{ g}}$
 $\therefore i = 0.504$

Benzoic acid exists as dimer, therefore

$$\therefore i = \frac{\text{Number of moles at equilibrium}}{\text{Number of moles initially}}$$

$$\therefore 0.504 = \frac{1 - (\alpha/2)}{1}$$

$$\alpha = 0.992$$

Therefore, degree of association of benzoic acid in benzene is 99.2%.

ILLUSTRATION 2.181

0.6 mL of acetic acid (CH₃COOH) having density 1.06 g mL⁻¹ is dissolved in 1 L of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the Van't Hoff factor and dissociation constant of the acid. ($K_{\rm f}$ for $H_2O = 1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$

Sol.
$$Mw_2$$
 (CH₃COOH) = 60 g mol⁻¹,
 W_2 (CH₃COOH) = $V \times d$
= 0.6 × 1.06
= 0.636 g

Molality (m) of acetic acid,

$$= \frac{W_2 \times 1000}{Mw_2 \times W_1} \qquad \begin{bmatrix} 1 \text{ L of H}_2\text{O} = 1000 \text{ g} \\ \text{Since } d_{\text{H}_2\text{O}} = 1 \text{ g mL}^{-1} \end{bmatrix}$$

$$= \frac{0.636 \times 1000}{60 \times 1000} = 0.0106 \text{ mol kg}^{-1}$$

Substituting the values in the equation

$$\Delta T_{\rm f} = iK_{\rm f} \times m$$

0.0205 K = $i \times 1.86$ K kg⁻¹ mol⁻¹ × 0.0106 mol kg⁻¹
 $\therefore i = 1.041$

Acetic acid is a weak electrolyte and dissociates in water. Let x is the degree of dissociation of acetic acid. Thus,

$$\begin{array}{ccc} & CH_3COOH & \Longrightarrow & H^{\oplus} + CH_3COO^{\ominus} \\ \text{Initial} & c \text{ mol} & 0 & 0 \\ \text{Final} & c(1-x) & cx & cx \end{array}$$

Total number of moles at equilibrium

$$c(1-x) + cx + cx = c(1+x)$$

$$\therefore$$
 1.041 = 1 + $x \Rightarrow x = 0.041$

$$K_{a} = \frac{[CH_{3}COO^{\odot}][H^{\oplus}]}{[CH_{3}COOH]} = \frac{cx \times cx}{c(1-x)}$$
$$= \frac{0.0106m \times 0.041 \times 0.041}{(1.00-0.041)}$$
$$= 1.86 \times 10^{-5}$$

ILLUSTRATION 2.182

The freezing point depression of 0.001 m K_x [Fe(CN)₆] is 7.10 × 10⁻³ K. Determine the value of x. Given, $K_f = 1.86$ K kg mol⁻¹ for water.

Sol.
$$\Delta T_f = i \times K_f \times m$$

 $7.10 \times 10^{-3} = i \times 1.86 \times 0.001$
 $i = 3.817$
 $\alpha = \frac{i-1}{n-1}$
 $1 = \frac{3.817 - 1}{(x+1)-1}$
 $x = 2.817 \approx 3$

:. Molecular formula of the compound is $K_3[Fe(CN)_6]$.

ILLUSTRATION 2.183

A solution of non-volatile solute in water freezes at -0.80° C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and $K_{\rm f}$ for water is 1.86 degree per molal. Calculate the vapour pressure of this solution at 298 K.

Sol. Depression in freezing point,
$$\Delta T_{\rm f} = 0 - (-0.30) = 0.30$$

Now, $\Delta T_{\rm f} = K_{\rm f} \times m$
or $m = \frac{\Delta T_{\rm f}}{K_{\rm f}}$

$$m = \frac{0.80}{1.86} = 0.430$$

According to Raoult's law,

$$\frac{P^{\circ}-P}{P^{\circ}}=\chi_{\rm B}=\frac{n_{\rm B}}{n_{\rm A}+n_{\rm B}}\,,$$

or
$$\frac{P^{\circ} - P}{P^{\circ}} = \frac{n_{\rm B}}{n_{\rm A}}$$

(for dilute solution)

Here,
$$n_{\rm B} = 0.430$$
, $n_{\rm A} = \frac{1000}{18}$; $P^{\rm o} = 23.51$

$$\frac{23.51 - P}{23.51} = \frac{0.43 \times 18}{1000} = 0.00774$$

$$P = 23.51 - (23.51 \times 0.00774) = 23.32 \text{ mm Hg}$$

ILLUSTRATION 2.184

A 1.17% solution of NaCl is isotonic with 7.2% solution of glucose. Calculate the Van't Hoff factor of NaCl.

Sol. For isotonic solution, osmotic pressure should be same

$$\therefore \ \pi_{(\text{NaCl})} = \pi_{(\text{glucose})}$$

$$iC_1RT = C_2RT$$

$$iC_1 = C_2$$

$$i\left(\frac{1.17/58.5}{V}\right) = \frac{7.2/180}{V} \Rightarrow i = \frac{7.2 \times 58.5}{1.17 \times 180} = 2$$

ILLUSTRATION 2.185

Calculate the amount of NaCl which must be added to 100g water so that the freezing point, depressed by 2 K. For water $K_f = 1.86 \text{ K kg mol}^{-1}$.

Sol. NaCl is a strong electrolyte. It is completely dissociated in solution.

Degree of dissociation, $\alpha = 1$

NaCl
$$\longrightarrow$$
 Na $^{\oplus}$ + Cl $^{\odot}$

Number of particles after dissociation = $1 + (n-1)\alpha$

 $\frac{\Delta T_{\mathrm{obs}}}{\Delta T_{\mathrm{theo}}} = \frac{\text{Number of particles after dissociation}}{\text{Number of particles when there is no dissociation}}$

$$\frac{2}{\Delta T_{\text{theo}}} = 2$$

or
$$\Delta T_{\text{theo}} = 1$$

Let W g of NaCl be dissolved in 100 g of water.

So
$$\Delta T_{\text{theo}} = \frac{1000 \times K_f \times W_2}{W_1 \times M w_1}$$

or
$$W_2 = \frac{\Delta T_{\text{theo}} \times W_1 \times Mw_1}{1000 \times K_f} = \frac{1 \times 100 \times 58.5}{1000 \times 1.86} = 3.145 \text{ g}$$

ILLUSTRATION 2.186 0.002 molar solution of NaCl having degree of dissociation of 0.002 at 27°C has osmotic pressure equal to **a.** 0.94 bar **b.** 9.4 bar **c.** 0.094 bar **d.** 9.4×10^{-4} bar

$$c. \ \alpha = \frac{i-1}{n-1}$$

$$0.9 = \frac{i-1}{2-1}$$
; $i = 1.9$

Alternate method to calculate (i)

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= (2 \times 0.9) + (1 - 0.9)$$
 [$\alpha = 90\%$ or 0.9]

$$= 1.8 + 0.1 = 1.9$$

$$\pi = iCRT$$

$$= 1.9 \times 0.002 \times 0.082 \times 300$$

ILLUSTRATION 2.187

Osmotic pressure of 0.1 M aqueous solution of MgCl₂ at 300 K is 4.92 atm. What will be the percentage ionization of the salt?

a. 49%

b. 59%

c. 79%

d. 69%

Sol.

a.
$$\pi = iCRT$$

$$4.92 = i \times 0.1 \times 0.0821 \times 300$$

$$i = 1.90$$

$$\alpha = \frac{i-1}{n-1} = \frac{1.99-1}{3-1} = \frac{0.99}{2} = 0.49$$

Percentage of ionization = 49%

ILLUSTRATION 2.188

The Van't Hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg₂Cl₂ is 80% ionized in the solution)

a. 1.6

b. 2.6

d. 4.6

Sol. b. $Hg_2Cl_2 \Longrightarrow Hg_2^{2+} + 2Cl^{\odot}$

$$n = 3$$

$$\alpha = \frac{i-1}{n-1} \implies 0.8 = \frac{i-1}{3-1} \implies i = 2.6$$

Alternate method to calculate (i)

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= (3 \times 0.8) + (1 - 0.8)$$
 [$\alpha = 80\%$ or 0.8]

$$= 2.4 + 0.2 = 2.6$$

ILLUSTRATION 2.189

A certain substance A tetramerizes in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is (K_f) for water $= 1.86 \text{ Km}^{-1}$).

a. 124

b. 32

c. 50

d. 62

Sol.

$$\mathbf{d.} \ \alpha = \frac{1-i}{1-\frac{1}{-}}$$

$$0.8 = \frac{1-i}{1-\frac{1}{4}} \Rightarrow i = 0.4$$

Given that $4A \longrightarrow A_{\Delta}$

Alternate method to calculate (i)

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= \left(\frac{1}{4} \times 0.8\right) + (1 - 0.8) \qquad [\alpha = 80\% \text{ or } 0.8]$$

$$= 0.2 + 0.2 = 0.4$$

$$\Delta T = iK_{\rm f} \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{W_{\rm B} \times 1000}{Mw_{\rm B} \times W_{\rm A}}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{Mw_{\text{B}} \times 100} \implies Mw_{\text{B}} = 62$$

ILLUSTRATION 2.190

When cells of skeletal vacuoles of a frog were placed in a series of NaCl solutions of different concentration solution at 25°C, it was observed microscopically that they remained unchanged in 0.7% solution, shrank in a more concentrated and swelled in more dilute solutions. Water freezes from the 0.7% salt solutions at -0.406°C. What is the osmotic pressure of the cell cytoplasm $(K_{\rm f} = 1.86 \text{ K kg mol}^{-1})$ at 25°C.

Sol.
$$\Delta T_{\rm f} = K_{\rm f} \times i \times C_{\rm m}$$

$$= K_{\rm f} \times (1 + \alpha) \times \frac{W}{m} \times \frac{1000}{W \text{ (in g)}}$$

$$\therefore 0.406 = 1.86 \times (1 + \alpha) \times \frac{0.7}{58.5} \times \frac{1000}{99.3}$$

$$\therefore 1 + \alpha = \frac{0.4 \times 58.5 \times 100}{1.86 \times 0.7 \times 1000}$$

Assuming dilute solution

$$100 \text{ g H}_2\text{O} = 100 \text{ mL H}_2\text{O} = 0.1 \text{ L solutions}$$

$$\pi = i \times \frac{n_2}{V} \times RT = (1 + \alpha) \times \frac{W_2}{Mw_2} \times \frac{1}{V} \times RT$$

$$= \frac{0.406 \times 58.5 \times 100}{1000 \times 1.86 \times 0.7} \times \frac{0.7}{58.5} \times \frac{1}{0.1} \times 0.082 \times 298$$

= 5.34 atm

ILLUSTRATION 2.191

A saturated solution of Mg(OH), has a vapour pressure of 759.5 mm at 373 K. Calculate the solubility and $K_{\rm sp}$ of Mg(OH)₂. (Assume molarity equals molality)

Sol. $P_{\rm S} = 759.5 \, \rm mm$

$$P_{\rm H_2O}^{\circ} = 760 \text{ mm at } 373 \text{ K}$$

$$\frac{\Delta P}{P^{\circ}} = \frac{0.5}{760} = i\chi_{2}$$

$$\therefore i\chi_{2} = 6.5 \times 10^{-4} (i = 3)$$

$$\chi_{2} = 2.16 \times 10^{-4}$$
Find molality \approx molarity
$$m = \frac{\chi_{B} \times 1000}{(1 - \chi_{B}) \times Mw_{1}} = 0.012 \text{ mol kg}^{-1}$$

$$Mg(OH)_{2} \rightleftharpoons Mg^{2+} + 2OH^{\odot}$$

$$i = 3$$

$$S = 0.012 \text{ mol L}^{-1}$$

$$K_{SP} = 4S^{3}$$

$$= 4 \times (0.012)^{3}$$

$$= 6.8 \times 10^{-6}$$

ILLUSTRATION 2.192

The freezing point of an aqueous solution of KCN containing 0.1892 mol kg⁻¹ was found to be -0.704°C. On adding 0.095 mol of Hg(CN)₂, the freezing point of the solution was found to be -0.530°C. If the complex formation takes place according to the following equation:

$$Hg(CN)_2 + nKCN \Longrightarrow K_n[Hg(CN)_{n+2}]$$

What is the formula of the complex? $[K_f (H_2O) \text{ is } 1.86 \text{ K kg mol}^{-1}]$

Sol. For KCN, $i = 1 + \alpha$, where $\alpha =$ degree of dissociation

$$\Delta T_{\rm f} = K_{\rm f} \times i \times {\rm molarity}$$

$$0.704 = 1.86 \times i \times 0.1892$$

$$i = \frac{0.704}{1.86 \times 0.1892} = 2$$

or
$$1 + \alpha = 2$$

 $\alpha = 1$ indicates 100% ionization of KCN.

Now, $\Delta T_f = \text{(of the complex)} = 0.530$ °C

Molality of $Hg(CN)_2 = 0.095 \text{ mol kg}^{-1} = 0.095 \text{ m}$

$$K_n[Hg(CN)_{n+2}] \iff nK^{\oplus} + [Hg(CN)_{n+2}]^{-n}$$

1 0 0
(...initially moles)
1 - α α
(...moles after dissociation)

Here, $i = (1 - \alpha) + n\alpha + \alpha = 1 + n\alpha$

$$\alpha = 1$$

$$: i = 1 + n$$

$$\Delta T_f = K_f \times i \times \text{molality}$$

$$\Rightarrow 0.503 = 1.86 \times i \times 0.095$$

$$\Rightarrow i \approx 3$$

$$1 + n = 3$$
 or $n = 2$

Hence, the complex is $K_2[Hg(CN)_4]$.

ILLUSTRATION 2.193

One mole of triphenyl methanol lowers the freezing point of 1000 g of 100% sulphuric acid twice as much as one mole of methanol. Why?

Since the number of ions are doubled in Ph₃COH and depression is two times more for the same number of mole of each.

ILLUSTRATION 2.194

A 0.025 m solution of monobasic acids has a freezing point of -0.060°C. What are K_a and pK_a of the acid? $(K_f = 1.36$ °C)

Sol.
$$\Delta T_f = iK_f m$$
; $0.060 = i \times 1.86 \times 0.25$
 $\therefore i = 1.29$
HA \Longrightarrow H^{\oplus} + A^{\oplus}
 $(1-\alpha)$ α α
 $\therefore i = 1 - \alpha + \alpha = 1 + \alpha$
 $\therefore \alpha = 0.29$
 $K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.29)^2}{(1-0.29)} = 3 \times 10^{-3} \Rightarrow pK_a = 2.5$

ILLUSTRATION 2.195

A 0.2 molal solution of KCl freezes at -0.68° C. If K_{i} for \mathbb{H}^{0} is 1.86, the degree of dissociation of KCl is

Sol. b.
$$\Delta T = i \times K_f \times m$$

 $0.68 = i \times 1.86 \times 0.2$
 $i = 1.83$
 $\alpha = \frac{i-1}{n-1} = \frac{1.83-1}{2-1} = 0.83$
Ionization = 83%

ILLUSTRATION 2.196

A mixture of 0.1 mol of Na₂O and 0.1 mol of BaO is dissolved in 1000 g of H₂O. Calculate the vapour pressure of solution if 373 K.

Sol. Na₂O and BaO both are ionic compounds and are completely ionized to give 3 and 2 ions, respectively,

(i)
$$Na_2O \longrightarrow 2Na^{\oplus} + O^{2-} (i = 3)$$

(ii) BaO
$$\longrightarrow$$
 Ba²⁺ + O²⁻ ($i = 2$)

$$P^{\circ} - \frac{P_{s}}{P^{\circ}} = i\chi_{\text{Na}_{2}\text{O}} + i\chi_{\text{BaO}}$$

$$\frac{760 - P_{s}}{760} = 3 \times \frac{0.1}{0.1 + 0.1 + 55.5} + 2 \times \frac{0.1}{0.1 + 0.1 + 55.5}$$

$$P_s = 753.21 \text{ mm Hg}$$

Alternatively

Total number of ions = $5 \times 0.1 = 0.5$

$$\frac{P^{\circ} - P_{\rm s}}{P_{\rm s}} = \frac{n_2}{n_1} = \frac{0.5}{55.5} = 0.009$$

$$\frac{760 - P_{\rm s}}{P_{\rm s}} = 0.009$$

Solve for $P_s \Rightarrow 753.21 \text{ mm Hg.}$

ILLUSTRATION 2.197

1575.2 g of C₆H₅OH (phenol) is dissolved in 960 g of a solvent of $K_f = 14 \text{ K kg mol}^{-1}$. If the depression in freezing point is 7 K, then find the percentage of phenol that dimerizes.

Sol.
$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

 $i = 1 - \alpha + \frac{\alpha}{2} = \frac{\Delta T_f}{K_f \cdot m} \Rightarrow \alpha = 0.8$

ILLUSTRATION 2.198

Following are equimolal aqueous solutions:

b. 1 m KCl

d. 1 m Na₃PO₄

Arrange them in increasing

i. Boiling point

ii. Freezing point

iii. Osmotic pressure

iv. Vapour pressure

While analysing the colligative properties, if the density of the solution is not given, take the molarity of the solution same as molality and vice-versa.

In such type of questions, always assume 100% dissociation for the ionic solutes until and unless specified

Solute	Ionization	i i
a. Urea	No	1
b. KCl	K [⊕] + Cl [⊙]	2
c. MgCl ₂	Mg ²⁺ + 2Cl [⊙]	3
d. Na ₃ PO ₄	$3Na^{\oplus} + PO_4^{3-}$	4

i. Boiling point of solution

$$T_{\rm b} = T_{\rm b}^{\,\circ} + (\Delta T_{\rm b})$$

$$\Delta T_{\rm b} = i(K_{\rm b}m)$$

Thus, greater the value of i, greater the value of ΔT_b and boiling point of solution.

ii. Freezing point of solution

$$T_{\rm f} = T_{\rm f}^{\,\circ} - (\Delta T_{\rm f})$$

$$\Delta T_{\rm f} = i(K_{\rm f} m)$$

Thus, greater the value of i, greater the value of ΔT_f but smaller the value of freezing point.

iii.Osmotic pressure (π)

$$\pi = iCRT$$

Thus, greater the value of i, larger the value of osmotic pressure.

iv. Vapour pressure of solution

$$\frac{\Delta P}{P_{\rm A}^{\circ}} = i\chi_{\rm B} \text{ or } \frac{\Delta P}{P_{\rm A}^{\circ}} = i\frac{n_{\rm B}}{n_{\rm A} + n_{\rm B}} \approx \frac{n_{\rm B}}{n_{\rm A}}$$

Thus, greater the value of i, greater the value of ΔP .

Hence, smaller the value of vapour pressure of solution.

ILLUSTRATION 2.199

To 250 mL of water, x g of acetic acid is added. If 11.5% of acetic acid is dissociated, the depression in freezing point comes out 0.416. What will be the value of x if K_f (water) = 1.86 K kg⁻¹ mol⁻¹ and density of water is 0.997 g mL-1

Sol. Given that: $W_2 = x$ g; $\Delta T_f = 0.416$; $\alpha = 0.115$

$$\alpha = \frac{i-1}{n-1}$$

So,
$$i = 1.115$$

$$\Delta T_{\rm f} = i \times m \times K_{\rm f}$$

$$\Delta T_{\rm f} = i \times \frac{W_2 \times 1000 \times K_{\rm f}}{Mw_2 \times W_1}$$

$$0.416 = 1.115 \times \frac{x \times 1000 \times 1.86}{60 \times 249.25}$$
 [W₂ = x g]

$$x = \frac{0.416 \times 60 \times 249.25}{1.115 \times 1000 \times 1.86} = 3 \text{ g}$$

ILLUSTRATION 2.200

A 250-mL water solution containing 8.19 g of sodium chloride at 300 K is separated from pure water by means of a semipermeable membrane. The pressure that must be applied above this solution in order to just prevent osmosis is (R = 0.0821 L)atm $mol^{-1} K^{-1}$)

- a. 13.80 atm
- b. 27.58 atm
- c. 23.34 atm
- d. 9.80 atm

Sol. b.
$$\pi = i \times C \times R \times T$$

[for NaCl,
$$i = 2$$
]

$$= 2 \times \frac{8.19}{58.5} \times \frac{1000}{250} \times 0.0821 \times 300 = 27.58 \text{ atm}$$

ILLUSTRATION 2.201

Calculate the osmotic pressure of a solution containing 0.02 mol of NaCl and 0.03 mol of glucose in 500 mL at 27°C.

2.58 Physical Chemistry

Sol.
$$C_{\text{effective}} = i_{\text{NaCl}} (=2) \times C_{\text{NaCl}} + i_{\text{Glucose}} (=1) \times C_{\text{Glucose}}$$

$$= \left(2 \times \frac{0.02}{500/1000} + 1 \times \frac{0.03}{500/1000}\right) M$$

$$= 0.14 \text{ M}$$

$$\Rightarrow \pi = C_{\text{eff}} RT = 0.14 \times 0.082 \times 300 \text{ atm} = 3.44 \text{ atm}$$

ILLUSTRATION 2.202

When dissolved in benzene, a compound C38H30 partially dissociates by the following equation:

 $C_{38}H_{30} \rightleftharpoons 2C_{19}H_{15}$. 25.6 g of $C_{38}H_{30}$ is dissolved in 400 g of benzene, the freezing point is lowered by 0.680°C. What percentage of $C_{38}H_{30}$ molecules have dissociated? ($K_f = 4.9$)

Sol.
$$\Delta T_{\rm f} = iK_{\rm f}m$$

$$i = \frac{\Delta T_{\rm f}}{K_{\rm f} \left(\frac{\frac{W_{\rm B}}{Mw_{\rm B}}}{W_{\rm A}} \times 1000\right)} = \frac{0.68}{4.9 \left(\frac{25.6}{486} \times 1000\right)} = 1.0538$$

Consider

$$C_{38}H_{30} \rightleftharpoons 2C_{19}H_{15}$$

$$1-x \qquad 2x$$

Total moles = 1 - x + 2x = 1 + x

$$i = \frac{\text{Total moles}}{\text{Initial moles}} = \frac{1+x}{1}$$

$$\Rightarrow 1.0538 = \frac{1+x}{1} \Rightarrow x = 0.0538$$

⇒ Percentage dissociation = 5.38%

ILLUSTRATION 2.203

Find the Van't Hoff factor of

- a. CH₃COOH in H₂O
- b. CH₃COOH in benzene

Sol.

a. CH₃COOH in water dissociates (as a weak acid)

$$CH_3COOH \rightleftharpoons CH_3COO^{\odot} + H^{\oplus} \Rightarrow i > 1$$

b. CH₃COOH in benzene (i.e., non-polar solvent) associates to form a dimer.

O.....HO

$$CH_3$$
— C — OH ... O = C — $CH_3 $\Rightarrow i < 1$$

ILLUSTRATION 2.204

A 0.1 M solution of potassium sulphate K_2SO_4 is dissolved to the extent of 80%. What would be its osmotic pressure at 27°C?

Sol. Use the result:
$$\pi = iCRT$$

Calculation of i:

$$K_2SO_4 \rightleftharpoons 2K^{\oplus} + SO_4^{2-}$$

$$\begin{matrix} 1 & 0 & 0 \\ 1-x & 2x & x \end{matrix}$$

Total moles =
$$1 - x + 2x + x = 1 + 2x$$

$$i = \frac{1+2x}{1} = \frac{1+2\times0.8}{1} = 2.6$$

$$\pi = 2.6 \times (0.1 \times 0.0821 \times 300) = 6.40 \text{ atm}$$

ILLUSTRATION 2.205

Van't Hoff factors of aqueous solutions of X, Y, and Z are 29 1.8, and 3.5, respectively. Which of the following statements is(are) correct?

a. BP:
$$X < Y < Z$$

b. FP:
$$Z < X < Y$$

c. Osmotic pressure:
$$X = Y = Z$$

d.
$$VP: Y < X < Z$$

Sol. Observed colligative property = $i \times \text{Normal colligative}$ property

a. Elevation in BP follows the order: Y < X < Z

 \Rightarrow BP following the order: Y < X < Z

b. Depression in FP follows the order:

$$Y < X < Z (T_f = T_f^{\circ} - \Delta T_f)$$

 \Rightarrow FP following the order: Z < X < Y

c. Osmotic pressure follows the order: Y < X < Z

d. Relative lowering in the VP follows:

VP follows the order: Z < X < Y

ILLUSTRATION 2.206

Acetic acid associates in benzene to form a dimer. 1.65 g d acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36°C. Calculate the Van't Hoff factor and degree of association of acetic acid.

$$(K_b \text{ for benzene} = 2.57^{\circ}\text{C m}^{-1})$$

Sol. Calculation of Van't Hoff factor:

First calculate the molecular mass from elevation in boiling point.

$$Mw_{\rm B} = K_{\rm b} \left(\frac{W_{\rm B}}{W_{\rm A} \Delta T_{\rm b}} \times 1000 \right)$$
$$= 2.57 \left(\frac{1.65}{100 \times 0.36} \times 1000 \right) = 117.8$$

$$\Rightarrow i = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}} = \frac{60}{117.8} = 0.509$$

Calculation of degree of association:

Let x = degree of association

Total moles =
$$1 - x/2$$

$$i = \frac{\text{Total moles}}{\text{Initial moles}} = \frac{1 - x/2}{1}$$

$$\Rightarrow 0.509 = \frac{1 - x/2}{1} \Rightarrow x = 0.982$$

ILLUSTRATION 2.207

The vapour pressure of benzene at 30°C is 164.88 mm of Hg. In 3 mol of benzene, when 6 g of acetic acid was dissolved, the vapour pressure of the solution became 162.04 mm of Hg.

- a. Van't Hoff factor
- b. The degree of association of acetic acid in benzene at 30°C
- Using the relation for lowering in vapour pressure and considering the Van't Hoff factor (i), we have

$$\frac{\Delta P}{P_{A}^{\circ}} = i\chi_{B}$$

$$\Rightarrow \frac{(164.88 - 162.04)}{164.88} = i\left(\frac{0.1}{0.1 + 3}\right)$$

Hence, acetic acid associates in benzene

$$2(CH_3COOH) \iff (CH_3COOH)_2$$

$$1 - \alpha \qquad \alpha/2$$

$$\Rightarrow i = 1 - \alpha/2$$

$$\Rightarrow \alpha = 2(1 - 0.533) = 0.932$$

ILLUSTRATION 2.208

 $\Rightarrow i = 0.533$ (i.e., i < 1)

The freezing point of a solution containing 0.3 g of acetic acid in $43\,\mathrm{g}$ of benzene reduces by 0.3° . Calculate the Van't Hoff factor.

$$(K_{\rm f} \text{ for benzene} = 5.12 \text{ K kg mol}^{-1})$$

Sol. The given values are

$$W_{\rm B} = 0.3 \text{ g}; \qquad \Delta T_{\rm f} = 0.30$$

$$W_{\rm A} = 43 \text{ g}; \qquad \Delta K_{\rm f} = 5.12 \text{ K kg mol}^{-1}$$

Now, using formula

$$Mw_{\rm B} = \frac{K_f \times W_B \times 1000}{\Delta T_{\rm f} \times W_A}$$

$$\therefore Mw_{\rm B} = \frac{5.12 \times 0.3 \times 1000}{0.3 \times 43} = 120 \text{ g mol}^{-1}$$

Normal molar mass = 60

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{60}{120} = 0.5$$

ILLUSTRATION 2.209

The freezing point of a 0.08 molal solution of NaHSO₄ is -0.372°C. Calculate the dissociation constant for the reaction.

$$HSO_4^{\ominus} \rightleftharpoons H^{\oplus} + SO_4^{2-}$$

 K_f for water = 1.86 K m⁻¹

Sol. NaHSO₄ dissociates as:

$$NaHSO_4 \longrightarrow Na^{\oplus} + HSO_4^{\ominus}$$

Since the concentration of NaHSO₄ is 0.08 m

$$[Na^{\oplus}] = 0.08 \ m; \ [HSO_4^{\ \odot}] = 0.08 \ m$$

Now, HSO₄ also dissociates as

$$[HSO_4^{\odot}] \iff H^{\oplus} + SO_4^{2-}$$

If α is the degree of dissociation, then after dissociation at equilibrium

$$[HSO_4^{\odot}] \rightleftharpoons 0.08(1-x)$$

$$[H^{\oplus}] = 0.08\alpha; [SO_4^{2-}] = 0.08\alpha$$

Total concentration of all ions (i.e., Na[⊕], H[⊕], HSO₄[⊙], and SO_4^{2-}

$$= 0.08 + 0.08(1 - \alpha) + 0.08\alpha + 0.08\alpha$$
$$= 0.16 + 0.08\alpha$$

$$∴ Van't Hoff factor, i = \frac{Observed moles of solute}{Normal moles of solute}$$
$$= \frac{0.16 + 0.08\alpha}{0.08} = 2 + \alpha$$

Now,
$$\Delta T_f = iK_f \times m$$

= $i \times 1.86 \times 0.088 = 0.1488i$

or
$$0.372 = 0.1488i$$

$$i = \frac{0.372}{0.1488} = 2.5$$

Thus,
$$2 + \alpha = 2.5$$
 or $\alpha = 0.5$

Dissociation constant for the reaction is

$$K = \frac{[H^{\oplus}][SO_4^{2-}]}{[HSO_4^{\odot}]}$$

$$[H^{\oplus}] = 0.08 \times 0.5 = 0.04$$

$$[HSO_4^{\circ}] = 0.08 \times (1 - 0.5) = 0.04$$

$$[SO_4^{\ 2-}] = 0.08 \times 0.5 = 0.04$$

$$K = \frac{(0.04) \times (0.04)}{(0.04)} = 4 \times 10^{-2}$$

ILLUSTRATION 2.210

Which of the following is (are) correct statements?

- i. 0.1 M CaCl₂ has higher boiling point than 0.1 M NaCl.
- ii. 0.05 M Al₂(SO₄)₃ has higher freezing point than 0.1 M $K_3[Fe(CN)_6].$
- iii. 0.1 M glucose exerts higher osmotic pressure than 0.08 M CH₃COOH (25% dissociated).
- iv. Vapour pressure of 0.05 M urea solution is greater than that of 0.05 M KCl solution.

The correct choice is

- a. i, iii
 - b. ii, iv
- c. i, ii, iii
- d. i, ii, iv

Sol.

d. T_h is higher if im is higher. T_f is higher if im is lower. π is higher if im is higher. VP is higher if im is lower.

$$CaCl_2$$
: $im = 3 \times 0.1$; $Al_2(SO_4)_3$: $im = 5 \times 0.05$;

Glucose: $im = 1 \times 0.1$; NaCl: $im = 2 \times 0.1$;

 $K_3[Fe(CN)_6]$: $im = 4 \times 0.1$;

CH₂COOH: $im = (1 + \alpha)m = 1.25 \times 0.08 = 0.1$

Urea: $im = 1 \times 0.05$; KCl: $im = 2 \times 0.05 = 0.1$

ILLUSTRATION 2.211

Under what conditions Van't Hoff factor (i) is

(a) equal to unity, (b) less than 1, and (c) greater than 1. Explain your answer.

Sol.

- a. When the solute does not undergo any dissociation or association in the solution, i.e., for non-electrolyte solutes.
- **b.** When the solute undergoes association in the solution.
- c. When the solute undergoes dissociation in the solution.

ILLUSTRATION 2.212

The freezing point of 0.20 M solution of week acid HA is 272.5 K. The molality of the solution is 0.263 mol kg⁻¹. Find the pH of the solution on adding 0.25 M sodium acetate solution.

 $K_{\rm f}$ of water = 1.86 K m⁻¹

Sol.
$$\Delta T_f = (273 - 272.5) = 0.5 \text{ K}$$

$$\Delta T_{\rm f} = iK_{\rm f}m$$

$$i = \Delta T_f / K_f m = 0.5/1.86 \times 0.263 = 1.022$$

$$HA \Longrightarrow H^{\oplus} +$$

$$1-\alpha$$
 α

$$i = 1 + \alpha$$

$$1.022 = 1 + \alpha \Rightarrow \alpha = 0.022$$

$$K_{\rm a} = C\alpha^2 = 0.2 \times (0.022)^2 = 9.6 \times 10^{-5}$$

$$\Rightarrow pK_2 = 4.0177$$

On adding 0.25 M NaA, buffer is formed

$$\therefore$$
 [Salt] = 0.25 M, [Acid] = 0.2 M

$$pH = pK_a + log [Salt/Acid] = 4.0177 + log(0.25/0.2)$$

$$=4.0177+0.0969=4.1146$$

0

α

ILLUSTRATION 2.213

Calculate the Van't Hoff factor (i) for the following if:

- i. 100% ionization or association takes place
- ii. 50% ionization or association takes place
 - a. S
- b. Se
- c. Te

- e. As i. Hg₂Cl₂
- f. Sb
- g. B

k. Be₂C

h. AlCl₃

d. P

- j. HgCl₂
- I. Al_4C_3

m. CaC₂

 \mathbf{n} . $\mathrm{Mg}_{2}\mathrm{C}_{3}$

Sol.

- i. (a, b, c)
 - S, Se, and Te exist as S_8 , Se_8 , and Te_8 molecules. So association takes place.

$$8S \rightleftharpoons S_8$$
, $8Se \rightleftharpoons Se_8$, $8Te \rightleftharpoons Te_8$

$$i=\frac{1}{8}$$

(d, e, f)

P, As, and Sb exist as P_4 , As₄, and Sb_4 molecules, s₁

$$4P \rightleftharpoons P_4$$
, $4As \rightleftharpoons As_4$, $4Sb \rightleftharpoons Sb_4$

$$i=\frac{1}{4}$$

g. B exists as B₁₂ molecule (icosahedron struchling 12 corners, and 20 faces), association takes $p|_{ace}$ $12B \rightleftharpoons B_{12}$

$$i=\frac{1}{12}$$

h. AlCl₃ exists as dimer in non-polar solvent, so association takes place.

$$2AlCl_3 \rightleftharpoons Al_2Cl_6$$

$$i = \frac{1}{2}$$

i. Hg_2Cl_2 (calomel) ionizes to give Hg_2^{2+} (mercurous) ion) and 2Cl[©] ions

$$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^{\odot}$$
 (So, $i = 3$)

j. HgCl₂ (corrosive sublimate) is a covalent compound and does not ionize. So i = 1.

Hg,Cl, is poisonous and antidote is white of an egg

(k, l) Be₂C and Al₄C₃ in H₂O gives CH₄ gas, so it contains C4- methinide ion.

$$Be_2C + 4H_2O \rightleftharpoons 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \rightleftharpoons 4Al(OH)_3 + CH_4$$

Hence, Be₂C and Al₄C₃ ionizes in solution 18 follows:

$$Be_2C \implies 2Be^{2+} + C^{4-} (i = 3)$$

$$Al_4C_3 \rightleftharpoons 4Al^{3+} + 3C^{4-} (i = 7)$$

m. CaC₂ gives (CH=CH) gas with H₂O. So it contains $(C^{\odot} \equiv C^{\odot} \text{ or } C_2^{2-} \text{ ion})$

$$CaC_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + CH \rightleftharpoons CH$$

So CaC₂ ionizes in solution as follows:

$$CaC_2 \rightleftharpoons Ca^{2+} + C_2^{2-} (i = 2)$$

n. Mg_2C_3 gives (CH_3-C) gas with H_2O .

So, it contains $CH_3C \equiv C^{\odot}$ or C_3^{4-} ions)

$$Mg_2C_3 + 4H_2O \rightleftharpoons 2Mg(OH)_2 + CH_3 - C = CH$$

Mg₂C₃ ionizes in solution as follows:

$$Mg_2C_3 \rightleftharpoons 2Mg^{2+} + C_3^{4-} (i = 3)$$

ii. (a, b, c)

For 50% association (α) = 50% or 0.5.

$$\begin{array}{ccc} & & & & & & & & \\ \text{Initial moles} & & 1 & & & 0 \\ \text{Final moles} & & 1-\alpha & & & \alpha / \end{array}$$

Total moles at equilibrium =
$$1 - \alpha + \frac{\alpha}{8}$$

$$i = \frac{\text{Total moles}}{\text{Initial moles}}$$

Alternate method

 $i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$

$$= \left(\frac{1}{8} \times 0.5\right) + (1 - 0.5) = \frac{0.5}{8} + 0.5$$

$$i = \frac{4.5}{8} = 0.5625$$

(d, e, f)

$$i = \frac{1 - \alpha + \frac{\alpha}{4}}{1}$$

$$= \frac{4 - 4\alpha + \alpha}{4}$$

$$= \frac{4 - 3\alpha}{4} = \frac{4 - 3 \times 0.5}{4} = \frac{2.5}{4} = 0.625$$

Alternate method

 $i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$

$$= \left(\frac{1}{4} \times 0.5\right) + (1 - 0.5)$$

$$=\frac{0.5}{4}+0.5=\frac{2.5}{4}=0.625$$

$$i = \frac{1 - \alpha + \frac{\alpha}{12}}{1}$$

$$= \frac{12 - 12\alpha + \alpha}{12}$$

$$= \frac{12 - 11\alpha}{12} = \frac{12 - 11 \times 0.5}{12} = \frac{6.5}{12} = 0.54$$

Alternate method

 $i = (Number of ions \times \alpha) + (1 - \alpha)$

$$= \left(\frac{1}{12} \times 0.5\right) + (1 - 0.5)$$
$$= \frac{0.5}{12} + 0.5 = \frac{6.5}{12} = 0.54$$

h.
$$\begin{array}{ccc} \text{Alcl}_3 & & \longrightarrow & \text{Al}_2\text{Cl}_6 \\ & \text{Initial moles} & 1 & & 0 \\ & \text{Final moles} & 1 - \alpha & & \alpha/2 \\ \end{array}$$

$$i = \frac{1 - \alpha + \frac{\alpha}{2}}{1} = 1 - \frac{\alpha}{2} = 1 - \frac{0.5}{2} = \frac{1.5}{2} = 0.75$$

Alternate method

 $i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$

$$= \left(\frac{1}{2} \times 0.5\right) + (1 - 0.5)$$
$$= \frac{0.5}{2} + 0.5 = \frac{1.5}{2} = 0.75$$

i.
$$Hg_2Cl_2 \Longrightarrow Hg_2^{2+} + 2Cl^{\odot}$$
Initial moles 1 0 0 0
Final moles $1-\alpha$ α 2α

$$i = \frac{1 - \alpha + \alpha + 2\alpha}{1} = 1 + 2\alpha = 1 + 2 \times 0.5 = 2$$

Alternate method

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

= $(3 \times 0.5) + (1 - 0.5)$

$$= 1.5 + 0.5 = 2$$

j. Since i = 1, it does not ionize.

k. Be₂C
$$\rightleftharpoons$$
 2Be²⁺ + C⁴⁻

$$1 \qquad 0 \qquad 0$$

$$1-\alpha \qquad 2\alpha \qquad \alpha$$

$$i = \frac{1-\alpha+2\alpha+\alpha}{1} = 1+2\alpha = 1\times2\times0.5 = 2$$

Alternate method

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= (3 \times 0.5) + (1 - 0.5)$$

$$= 1.5 + 0.5 = 2$$

1.
$$Al_4C_3 \rightleftharpoons 4Al^{3+} + 3C^{4-}$$

$$1 - \alpha \qquad 4\alpha \qquad 3\alpha$$

$$i = \frac{1 - \alpha + 4\alpha + 3\alpha}{1} = 1 + 6\alpha = 1 + 6 \times 0.5 = 4$$

Alternate method

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$=(7\times0.5)+(1-0.5)$$

$$= 3.5 + 0.5 = 4$$

m.
$$CaC_2 \iff Ca^{2+} + C_2^{2-}$$
 $1 \qquad 0 \qquad 0$
 $1-\alpha \qquad \alpha \qquad \alpha$

$$i = \frac{1 - \alpha + \alpha + \alpha}{1} = 1 + \alpha = 1 + 0.5 = 1.5$$

Alternate method

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= (2 \times 0.5) \pm (1 - 0.5)$$

$$= 1.0 + 0.5 = 1.5$$

$$i = \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\alpha = 1 + 2 \times 0.5 = 2$$

Alternate method

$$i = (Number of ions \times \alpha) + (1 - \alpha)$$

= $(3 \times 0.5) + (1 - 0.5)$
= $1.5 + 0.5 = 2$

CONCEPT APPLICATION EXERCISE 2.3

- 1. A certain solution of 1 molal benzoic acid in benzene has a freezing point of 3.1°C and a normal boiling point of 82.6°C. The freezing point of benzene is 5.5°C and its boiling point is 80.1°C. $K_{\rm f}$ of benzene = 5.12 K/m and $K_{\rm b} = 2.53$ K/m. Analyse the state of the solute (benzoic acid) at two temperatures and comment.
- 2. A solution is prepared by dissolving 1.5 g of a monoacidic base into 1.5 kg of water at 300 K which showed a depression in freezing point by 0.165°C. When 0.496 g of the same base is titrated, after dissolution, requires 40 mL of semimolar H₂SO₄ solution. If K_f of water is 1.86 K kg mol⁻¹, then select correct statement(s) out of the following (assuming molarity = molality):
 - a. The pH of the solution of weak base is 12.9.
 - **b.** Ionization constant of the base is 8×10^{-3} .
 - **c.** The osmotic pressure of the aqueous solution of base is 21.67 atm.
 - d. The base is 10% ionized in aqueous solution.
- 3. Tritium T^3 (an isotope of H) combines with fluorine to form weak acid TF, which gets ionized to give T^{\oplus} . A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at -0.372° C. If 600 mL of freshly prepared solution were allowed to start for 24.8 years, calculate the ionization constant of TF. (Given K_f for $H_2O = 1.86$)
- **4.** A dilute solution contains m mol of solute A in 1 kg of a solvent with molal elevation constant K_b , the solute dimerizes in solution as $2A \rightleftharpoons A_2$. Show that equilibrium constant for this dimer formation is

$$K = \frac{K_b(K_bm - \Delta T_b)}{(2\Delta T_b - K_bm)^2}$$
, where ΔT_b is the elevation in boiling

point for the given.

ANSWERS

- 1. Benzoic acid neither associate or dissociate at high temp.
- **2.** (a, b, c, d)
- 3. $k = 7.299 \times 10^{-3}$
- 4. Factual

Solved Examples

Henry's Law, Raoult's Law, Ideal and Non-Ideal Solutions

EXAMPLE 2.1

Calculate the mole fraction of solute in a dilute aqueous solution from which ice begins to separate out at -0.46°C. (K_f of H_2O = 1.86 K m⁻¹)

Sol.
$$\Delta T_f = K_f \times m \Rightarrow m = \frac{\Delta T_f}{K_f} = \frac{0 - (-0.46)}{1.86} = \frac{0.46}{1.86} = 0.247_{\text{fb}}$$

Use the relation,

$$m = \frac{n_2 \times 1000}{n_1 \times Mw_1}$$

$$\therefore \frac{n_2}{n_1} = \chi_2 = \frac{m \times Mw_1}{1000}$$
$$= \frac{0.247 \times 18}{1000}$$
$$= 0.004$$

EXAMPLE 2.2

The vapour pressure of water at 293 K is 17.51 mm. The lowering of vapour pressure of sugar is 0.0614 mm. Calculate

- a. The relative lowering of vapour pressure
- b. The vapour pressure of the solution
- c. The mole fraction of water

Sol. Here we are given that

Vapour pressure of water $(P^{\circ}) = 17.51 \text{ mm}$ Lowering of vapour pressure $(P^{\circ} - P_{\circ}) = 0.0614 \text{ mm}$

a. Relative lowering of vapour pressure

$$\frac{P^{\circ} - P_{\rm s}}{P^{\circ}} = \frac{0.0614}{17.51} = 0.00351$$

b. Vapour pressure of the solution

$$P_{\rm s} = P^{\circ} - (P^{\circ} - P_{\rm s}) = 17.51 - 0.0614 = 17.4486 \,\mathrm{mm}$$

c. To calculate the mole fraction of water

By Raoult's law
$$= \frac{P^{\circ} - P_{s}}{P^{\circ}}$$
$$= \frac{n_{2}}{n_{1} + n_{2}}$$
$$= \chi_{2}, \text{ mole fraction of solute}$$

i.e.,
$$\chi_2 = \frac{P^\circ - P_s}{P^\circ} = 0.00351$$

.. Mole fraction of solvent (water),

$$\chi_1 = 1 - \chi_2 = 1 - 0.00351 = 0.99649$$

EXAMPLE 2.3

The vapour pressure of a 5% aqueous solution of a non-volatile organic substance at 373 K is 745 mm. Calculate the molecular mass of the solute.

Sol. 5% aqueous solution of the solute implies that 5 g of the solute are present in 100 g of the solution, i.e.,

Weight of solute $(W_2) = 5 g$

Weight of solution = 100 g

$$\therefore$$
 Weight of solvent $(W_1) = 100 - 5 = 95 \text{ g}$

Further as the solution is aqueous, it means that the solvent is water and we know that vapour pressure of pure water 373 K = 760 mm

Vapour pressure of the solution at 373 K $(P_s) = 745 \text{ m}^{\text{m}}$ (given)

Molecular mass of solvent (water), $Mw_1 = 18$ Molecular mass of solute, Mw_2 = To be calculated Using the formula for dilute solutions, viz

$$\frac{P^{\circ} - P_{\rm s}}{P^{\circ}} = \frac{n_2}{n_1} = \frac{W_2 / Mw_2}{W_1 / Mw_1}$$
We get
$$\frac{760 - 745}{760} = \frac{5 / Mw_2}{95 / 18} = \frac{5 \times 18}{95 \times Mw_2}$$
or
$$Mw_2 = \frac{5 \times 18 \times 760}{15 \times 95} = 48$$

EXAMPLE 2.4

At 298 K, the vapour pressure of water is 23.75 mm Hg. Calculate the vapour pressure at the same temperature over 5% aqueous solution of urea. [CO (NH₂)₂].

$$\frac{P^{\circ} - P_{\rm s}}{P^{\circ}} = \frac{n_2}{n_1} = \frac{W_2 / M w_2}{W_1 / M w_1} = \frac{W_2 \times M w_1}{M w_1 \times W_1}$$

Substituting the values, we get

$$\frac{23.75 - P_s}{23.75} = \frac{5}{60} \times \frac{18}{95}$$

$$23.75 - P_s = \frac{5}{60} \times \frac{18}{95} \times 23.75$$
or $23.75 - P_s = 0.375 \implies P_s = 23.375$ mm

EXAMPLE 2.5

Liquids A and B form an ideal mixture, in which the mole fraction of A is 0.25. At temperature T, a small quantity of the vapour in equilibrium with the liquid is collected and condensed. This process is repeated for a second time with the first condensate. The second condensate now contains 0.645 mole fraction of A. Calculate the ratio $(P_A^{\circ}/P_B^{\circ})$. What will be the mole fraction of B in the third condensate?

Sol. Mole fraction of A
$$(\chi_A) = 0.25$$

Mole fraction of B (χ_B) = 0.75

After first condensation

Partial pressure of A $(p_A) = P_A^{\circ} \chi_A = P_A^{\circ} \times 0.25$

Partial pressure of B $(p_B) = P_B^{\circ} \times 0.75$

$$\frac{p_{A}}{p_{B}} = \frac{P_{A} \circ}{P_{B} \circ} \times \frac{0.25}{0.75}$$
After second condensation

Mole fraction of A $(\chi_A) = 0.645$

Mole fraction of B $(\chi_B) = 1 - 0.645 = 0.355$

Ratio of partial pressures

$$\frac{p_{A''}}{p_{A''}} = \left(\frac{P_{A}^{\circ}}{P_{B}^{\circ}}\right)^{2} \times \frac{0.25}{0.75} = \frac{0.645}{0.345}$$

$$\therefore \left(\frac{P_{\rm A}{}^{\circ}}{P_{\rm B}{}^{\circ}}\right)^2 = \frac{0.645}{0.355} \times \frac{0.75}{0.25}$$

$$\therefore \frac{P_{\rm A}^{\circ}}{P_{\rm B}^{\circ}} = 2.33$$

After third condensation

$$\frac{p_A^{""}}{p_A^{""}} = \left(\frac{P_A^{\circ}}{P_B^{\circ}}\right)^3 \times \frac{0.25}{0.75} = (2.33)^3 \times \frac{0.25}{0.75} = 4.242$$

: Mole fraction of B

$$\frac{p_{\rm B}^{""}}{p_{\rm A}^{""} + p_{\rm B}^{""}} = \frac{1}{5.42} = 0.191 = \text{Mole fraction of B}$$

EXAMPLE 2.6

A certain solution of 1 m benzoic acid in benzene has a freezing point of 3.1°C and a normal boiling point of 82.6°C. The freezing point of benzene is 5.5°C and its boiling point is 80.1°C. Analyze the state of the solute (benzoic acid) at two temperatures and comment.

Sol. Case I

Calculate Van't Hoff factor in two cases:

$$i = \frac{\Delta T_{\rm f}}{K_{\rm f} \times m} = \frac{(5.5 - 3.1)}{5.12 \times 1} = 0.469$$

So benzoic acid associates in benzene at low temperature since $i \approx 0.5$, so it forms dimer.

Case II

$$i = \frac{\Delta T_{\rm f}}{K_{\rm f} \times m} = \frac{(82.6 - 80.1)}{2.53 \times 1} = 0.99$$

So benzoic acid neither associates nor dissociates at high temperature.

Note: If i > 1, then solute dissociates.

EXAMPLE 2.7

In a study of aqueous solution of thorium nitrate, the freezing point depression of 0.0703 °C is observed for a 9.6 mmol kg⁻¹ of the solution. How many ions are present in one thorium nitrate unit? $(K_f \text{ for } H_2O = 1.86 \text{ K m}^{-1})$

Sol. Van't Hoff factor
$$(i) = \frac{\text{Total number of ions in solution}}{\text{Number of ions initially}}$$

or
$$i = \frac{\Delta T_{\rm f}}{K_{\rm f} \times m} = \frac{0.0703}{1.86 \times 9.6 \times 10^{-3}}$$

= 3.9 \approx 4.

i = 4 or total number ions/unit

EXAMPLE 2.8

Two liquids A and B form an idea solution. What will be the vapour pressure at 27°C of a solution having 1.5 mol of A and 4.5 mol of B? The vapour pressure of A and B at 27°C is 0.116 atm and 0.140 atm, respectively.

Sol.
$$n_A = 1.5 n_B = 4.5$$

$$\chi_{\rm A} = \frac{1.5}{1.5 + 4.5} = \frac{1.5}{6.0} = \frac{1}{4}$$

$$\chi_{B} = 1 - \frac{1}{4} = \frac{3}{4}$$

$$P = P_{A} \circ \chi_{A} + P_{B} \circ \chi_{B} = 0.116 \times \frac{1}{4} + 0.14 \times \frac{3}{4}$$

$$P = 0.029 + 0.105 = 0.134$$

Azeotropic Mixture, Solubility of partially Miscible liquids, Colligative Properties

EXAMPLE 2.9

A 4% solution of sucrose $C_{12}H_{22}O_{11}$ is isotonic with 3% solution of an unknown organic substance. Calculate the molecular mass of the unknown substance.

Sol. Since the two solutions are isotonic, they must have same concentrations in moles/litre.

For sucrose solution, we have concentration

=
$$4 \text{ g/100 cm}^3 \text{ (given)}$$

= $40 \text{ g L}^{-1} = \frac{40}{342} \text{ mol L}^{-1}$

(Molecular mass of sucrose $C_{12}H_{22}O_{11} = 342$)

For unknown substance, suppose m is the molecular mass, then concentration = $3 \text{ g}/100 \text{ cm}^3$ (given)

$$= 30 \text{ g L}^{-1} = \frac{30}{Mw} \text{ mol L}^{-1}$$

Thus, we have $\frac{30}{Mw} = \frac{40}{342}$

$$Mw = \frac{30 \times 342}{40} = 256.5$$

EXAMPLE 2.10

Calculate the osmotic pressure of a solution obtained by mixing 100 cm^3 of 1.5% solution of urea (mol. mass = 60) and 100 cm^3 of 3.42% solution by cane sugar (mol. mass = 342) at 20°C . (R = 0.082 litre atm/deg/mole)

Sol. After mixing total volume of the solution

$$= 100 + 100 = 200 \text{ cm}^3$$

Osmotic pressure due to the urea in the solution.

1.5~g of urea which was present originally in $100~cm^3$ is now present in $200~cm^3$, i.e., in the final solution.

$$Mw_1 = Mw_{\text{urea}} = \frac{W_2 \times 1000}{Mw_2 \times \text{vol. of sol.}} = \frac{1.5 \times 1000}{60 \times 200} = 0.125$$

 $Mw_2 = Mw_{\text{sugar}} = \frac{3.42 \times 1000}{342 \times 200} = 0.05$

$$\pi = (Mw_1 + Mw_2)RT$$

= (0.125 + 0.05) × 0.082 × 293 = 4.2 atm

EXAMPLE 2.11

A solution containing 6 g of a solute dissolved in 250 cm³ of water gave an osmotic pressure of 4.5 atm at 27°C. Calculate the boiling point of the solution. The molal elevation constant for water is 0.52°C per 1000 g.

Sol. Van't Hoff equation for osmotic pressure is $\pi V = nRT$

$$4.5 \times 0.25 = n \times 0.0821 \times 300$$

or
$$n = \frac{4.5 \times 0.25}{0.0821 \times 300} = 0.0457 \text{ mol}$$

i.e., 0.0457 mol of the solute is present in 250 mL $_{06}$ W_{4|6} or 250 g of water.

or 250 g of water.

$$\therefore \text{ Molality of the solution } m = \frac{0.0457}{250} \times 1000$$

$$= 0.1828$$

$$\Delta T_{\rm b} = K_{\rm b} \cdot m = 0.52 \times 0.1828 = 0.095$$
°C

.. Boiling point of solution

$$(T_s) = T_0 + \Delta T_b = 100 + 0.095 = 100.095$$
°C

EXAMPLE 2.12

A solution containing 25.6 g of sulphur, dissolved in $1000 \, \mathrm{g}$ of naphthalene whose melting point is $80.1 \, ^{\circ}\mathrm{C}$ gave a freezing point lowering of $0.680 \, ^{\circ}\mathrm{C}$. Calculate the formula of sulphur (K_{f} for naphthalene = $6.8 \, \mathrm{K} \, \mathrm{m}^{-1}$)

Sol.
$$\Delta T_{\rm f} = iK_{\rm f}m$$

 $0.68 = i \times 6.8 \times \frac{25.6 \times 1000}{32 \times 1000}$

i = 1/8

Since i is less than 1, therefore, S is associated, i.e., 8 moles of S are associated as shown below

$$8S \rightleftharpoons S_8$$

Therefore, the molecular formula of sulphur is S₈.

EXAMPLE 2.13

A mixture which contains 0.550 g of camphor and 0.090 g of an organic solute melts at 161°C. The solute contains 93.75% C and 6.25% H by weight. What is the molecular formula of compound? K_f for camphor is 37.5°C mol⁻¹ kg. The melting point of camphor is 209°C.

Sol. Given,

$$\Delta T = 209 - 161 = 48$$
°C

 $W_2 = 0.09 \text{ g (organic solute)}$

 $W_1 = 0.55 \text{ g (camphor)}$

 $K_{\rm f} = 37.5^{\circ} {\rm C \ mol^{-1} \ kg}$

$$\Delta T = \frac{1000 \times K_{\rm f} \times W_2}{Mw_2 \times W_1}$$

$$48 = \frac{1000 \times 37.5 \times 0.09}{Mw_2 \times 0.55}$$

$$Mw_2 = 127.84$$

%	(%/Atomic weight) value	Value/Lowest value		
C = 93.75	$\frac{93.75}{12} = 7.8125$	$\frac{6.25}{1} = 6.25$		
H = 6.25	$\frac{7.8125}{6.25} = 1.25$	$\frac{6.25}{6.25} = 1$		

∴ C: H:: 1.25:1 or 5: 4

: Molecular formula is $(C_5H_4)_n$ and $n = \frac{127.84}{64} \approx 2$

 \therefore Molecular formula of solute is $(C_5H_4)_2 = C_{10}H_8$

EXAMPLE 2.14

A solution containing 0.1 mol of naphthalene and 0.9 mol of benzene is cooled out until some benzene freezes out. The solution is then decanted off from the solid and warmed upto 353 K where its vapour pressure was found to be 670 mm. The freezing point and boiling point of benzene are 278.5 K and 353 K respectively, and its enthalpy of fusion is 10.67 kJ mol⁻¹. Calculate the temperature to which the solution was cooled originally and the amount of benzene that must have frozen out. Assume ideal behaviour.



Sol. Given, mole of napthalene $(n_2) = 0.1$

Mole of benzene $(n_1) = 0.9$

Vapour pressure of benzene $(P^{\circ}) = 760 \text{ mm}$

Boiling temperature of benzene = 353 K

Vapour pressure of solution = 670 mm

Freezing point of benzene = 278.5 K

Enthalpy of fusion $(\Delta_{\text{fus}}H) = 10.67 \text{ kJ mol}^{-1}$

Using Raoult's law:

$$\frac{P^{\circ} - P_{s}}{P_{s}} = \frac{W_{2} \times Mw_{1}}{Mw_{2} \times W_{1}}$$

 $W_2 = Weight of naphthalene$

 Mw_2 = Molecular weight of naphthalene

 Mw_1 = Molecular weight of benzene

 W_1 = Weight of benzene

$$\frac{760 - 670}{670} = \frac{0.1 \times 78}{W_1}$$
; (Mole of naphthalene = $\frac{W_2}{Mw_2} = 0.1$)

 $W_1 = 58.06 \text{ g}$

Weight of benzene in original solution (W_B)

= Mole × Molecular weight

$$= 0.9 \times 78 = 70.2 \text{ g}$$

Amount of benzene frozen out = 70.2 - 58.06 = 12.14 g

Now,
$$\Delta T_{\rm f} = K_{\rm f} \times m = \frac{RT^2m}{1000 \, \Delta H}$$

$$= \frac{8.314 \times (278.5)^2}{1000 \times \frac{10.67 \times 10^3}{78}} \times \frac{1000 \times 0.1}{58.06}$$

$$= 8.11 \, \text{K}$$

Thus, original solution must have been cooled to = 278.5 - 8.11 = 270.39 K

EXAMPLE 2.15

A 10 g mixture of glucose and urea present in 250 mL solution shows the osmotic pressure of 7.4 atm at 27°C. Calculate % composition of mixture.

Sol. Let the mixture contains a g glucose and b g urea.

$$\therefore a+b=10 \qquad ...(i)$$

From $\pi V = nRT$

Also,
$$7.4 \times \frac{250}{1000} = \left[\frac{a}{180} + \frac{b}{60} \right] \times 0.0821 \times 300$$

$$3a + b = 13.52$$
 ...(ii)

Solving Eqs. (i) and (ii), we get

$$a = 1.76 \text{ g}$$

$$b = 8.24 \text{ g}$$

% of glucose =
$$\frac{1.76}{10} \times 100 = 17.6$$

% of urea =
$$\frac{8.24}{10} \times 100 = 82.4$$

EXAMPLE 2.16



A tube of uniform cross-sectional area 1 cm2 is closed at one end with semi-permeable membrane. A solution of 5 g glucose per 100 mL is placed inside the tube and is dipped in pure water at 27°C. When equilibrium is established, calculate:

- a. The osmotic pressure of solution.
- b. The height developed in vertical column.

Assume the density of final glucose solution 1 g mL-1

Sol.

a.
$$\pi V = \frac{W}{Mw}RT$$

Given that $W = 5$ g, $V = \frac{100}{1000}$ L

$$T = 300 \text{ K}$$
, $Mw = 180 \text{ (Mw of glucose} = 180)$

$$\pi = \frac{5 \times 1000 \times 0.0821 \times 300}{180 \times 100} = 6.842 \text{ atm}$$

b.
$$\pi = hdg$$

Given
$$d = 1$$
 g cm⁻³ = 10^3 kg m⁻³
 $\pi = 6.842 = 6.842 \times 1.01 \times 10^5$ N m⁻²
 $g = 9.81$ m s⁻²
 $\therefore 6.841 \times 1.01 \times 10^5 = h \times 10^3 \times 9.81$

$$h = \frac{6.841 \times 1.01 \times 10^5}{9.81 \times 10^3} = 70.43 \text{ m}$$

EXAMPLE 2.17

a. 191

The freezing point of a 3% (by weight) aqueous solution of A is equal to the freezing point of 9% (by weight) aqueous solution of B. If the molecular weight of A is 60, then the molecular weight of B will be

Sol.

a. Freezing point of aqueous solution of A

b. 90

= Freezing point of water $-\Delta T_f$ of solution A Freezing point of aqueous solution of B

c. 45

d. 20

= Freezing point of water – ΔT_f of solution B

As freezing point of aqueous solution of A

= Freezing point of aqueous solution B

 $\therefore \Delta T_f$ of solution A = ΔT_f of solution B

$$K_{\rm f}m = K_{\rm f}m'$$

$$\frac{3/60}{97} \times 1000 = \frac{9/Mw_{\rm B} \times 1000}{91}$$

$$\therefore Mw_{\rm B} = 191$$

EXAMPLE 2.18

2.5 g of a substance is present in 200 mL of solution showing the osmotic pressure of 60 cm Hg at 15°C. Calculate the molecular weight of substance. What will be the osmotic pressure if temperature is raised to 25°C?

Sol. Given that,
$$W_2 = 2.5 \text{ g}$$
, $V = \frac{200}{1000} \text{ L}$

$$\pi = \frac{60}{76} \underset{\circ}{\text{atm}}, T = 288 \text{ K}$$

$$\therefore \pi V = \frac{W_2}{Mw_2} RT$$

$$\frac{60}{76} \times \frac{200}{1000} = \frac{2.5}{Mw_2} \times 0.0821 \times 288 \Rightarrow Mw_2 = 374.38$$
Also, $\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$

$$\frac{60}{\pi_2} = \frac{288}{298} \Rightarrow \pi_2 = 62.08 \text{ cm}$$

EXAMPLE 2.19

Calculate osmotic pressure of a solution obtained by mixing 100 mL of 3.4% solution (weight/volume) of urea (molecular weight 60) and 100 mL of 1.6% solution (weight/volume) of cane sugar (molecular weight 342) at 20°C.

Sol.
$$\pi_1 V_1 = \frac{W_1}{Mw_1} RT_1$$
 for urea $\pi_2 V_2 = \frac{W_2}{Mw_2} RT_2$ for sugar

Since 100 mL of urea solution is mixed with 100 mL of cane sugar solution, and thus, the total volume becomes 200 mL in which 3.4 g urea and 1.6 g sugar is present.

$$\pi_1 \times \frac{200}{1000} = \frac{3.4}{60} \times 0.821 \times 293 = 6.82 \text{ atm}$$

$$\pi_2 \times \frac{200}{1000} = \frac{1.6}{342} \times 0.821 \times 293 = 0.56 \text{ atm}$$

$$\pi_3 \times \pi_{\text{total}} = \pi_1 + \pi_2 = 6.82 + 0.56 = 7.38 \text{ atm}$$

EXAMPLE 2.20

Which has maximum osmotic pressure at temperature T?

- a. 100 mL of 1 M urea solution
- b. 300 mL of 1 M glucose solution
- c. Mixture of 100 mL of 1 M urea solution and 300 mL of 1 M glucose solution
- d. All are isotonic

Osmotic pressure (π) depends upon the concentration of solution, i.e., $\pi = C_{\text{effective}} RT$

For (a), $C_{\text{effective}} = 1 \text{ M}$ (since it is non-electroly) solution)

solution) For (b), $C_{\text{effective}} = 1 \text{ M}$ (since it is a non-electroly/lip) solution)

For (c),
$$C_{\text{effective}} = \left[\frac{100}{100 + 300} \times 1 + \frac{300}{100 + 300} \times 1 \right]$$

= 1 N

EXAMPLE 2.21

CNS[©] ions give red colour with Fe³⁺ ions in aqueous solution as

$$Fe^{3+}(aq) + 3CNS^{\odot}(aq) \longrightarrow Fe(CNS)_3(aq)$$

red

If 0.1 M KCNS solution is separated from 0.1 M FeCl₃ solution by means of a semi-permeable membrane, red colour will appear on:

- a. FeCl₃ solution
- b. KCNS solution side
- c. Both sides
- d. Neither side

Sol. d.
$$Fe^{3+}(aq) + 3CNS^{\odot}(aq) \longrightarrow Fe(CNS)_3(aq)$$

 \Rightarrow Only solvent molecule moves from dilute solution concentrated solution.

$$0.1 \text{ M KCNS}$$
 $C_{\text{effective}} = 0.2 \text{ M}$
(Dilute)

 0.1 M FeCl_3 $C_{\text{effective}} = 0.2 \text{ M}$

vilute) (Concentrated)

So, no red colour will appear.

EXAMPLE 2.22

At 17°C, the osmotic pressure of sugar solution is 580 ton. The solution is diluted and the temperature is raised to 57°C, when the osmotic pressure is found to be 165 torr. The extent of dilution is

- a. 2 times
- **b.** 3 times
- c. 4 times

d. 5 times

Sol. c. Given

$$T_i = 17^{\circ}\text{C} = 290 \text{ K}; T_f = 57^{\circ}\text{C} = 330 \text{ K}$$

 $\pi_i = 580 \text{ torr} = \frac{580}{760} \text{ mm Hg}$
 $\pi_f = 165 \text{ torr} = \frac{165}{760} \text{ mm Hg}$

Using equation

$$\pi = CRT$$

$$\frac{580}{760} = C_{\rm i} \times R \times 290$$

...(i)

$$\frac{165}{760} = C_{\rm f} \times R \times 330$$

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{C_i}{C_f} = \frac{2}{1/2} = 4 \implies \text{Dilution} = 4 \text{ times}$$

EXAMPLE 2.23

Among the following, the solution which shows the lowest osmotic pressure is

- a. 0.10 M NaCl
- **b.** 0.05 M CaCl₂
- c. 0.04 M K₃[Fe(CN)₆]
- **d.** 0.03 M FeCl₃

a. $C_{\text{effective}} = 0.1 \times 2 = 0.2 \text{ M}$

a. $C_{\text{effective}}$ b. $C_{\text{effective}} = 0.05 \times 3 = 0.15 \text{ M}$

c. $C_{\text{effective}} = 0.04 \times 4 = 0.16 \text{ M}$

d. $C_{\text{effective}} = 0.03 \times 4 = 0.12 \text{ M}$

 $K_3[Fe(CN)_6] = 3K^{\oplus} + [Fe(CN)_6]^{3-}$

 $\Rightarrow C_{\text{effective}}$ is lowest for (d).

EXAMPLE 2.24

A 0.1 M solution of glucose (molecular weight 180 g mol⁻¹) and a 0.1 M solution of urea (molecular weight = 60 g mol⁻¹) are placed on the two sides of a semi-permeable membrane to equal heights. In this context, which of the following statements is correct?

- a. Glucose will flow across the membrane into the urea solution.
- b. Urea will flow across the membrane into the glucose solution.
- c. Water will flow across the membrane from the urea solution into the glucose solution.
- d. There will be no net movement across the membrane.

0.1 M glucose and 0.01 M urea

Since both the solutions have same concentrations, there will be no net movement of water molecules across the membrane.

EXAMPLE 2.25

If the radiator of an automobile contains 12 L of water, how much would the freezing point be lowered by the addition of 5 kg of prestone (glycol $C_2H_4(OH)_2$). How many kg of Zeron (methyl alcohol) would be required to produce the same result?

Sol. Given,

Weight of glycol $(W_2) = 5 \text{ kg} = 5000 \text{ g}$

Molecular weight of glycol $(Mw_2) = 62 \text{ g}$

 \therefore Weight of water = 12 kg $\left(\because \text{density} = \frac{V}{W}\right)$

Mole of glycol = $\frac{W_2}{Mw_2} = \frac{5000}{62} = 80.6$

Molality of solution (m) = $\frac{\text{Mole}}{\text{Weight of solvent}} = \frac{80.6}{12}$ = 6.7

Now, $\Delta T_f = K_f m = 1.86 \times 6.7 = 12 \text{ K}$

 \therefore Freezing point of solution = -12° C

With methyl alcohol, to get the same freezing point depression same number of moles are required.

 \therefore amount of methyl alcohol = Mole \times Mw = $80.6 \times 32 = 2579.2$ = 2.58 kg

EXAMPLE 2.26

If the boiling point of an aqueous solution is 100.1° C, what is its freezing point? Given $l_f = 80$, $l_v = 540$ cal g⁻¹ respectively, of H₂O.

Sol. $\Delta T_b = K_b \times m$ $\Delta T_f = K_f \times m$ $\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} = \frac{RT_b^2}{1000l_v} \times \frac{1000l_f}{RT_f^2}$ $\frac{\Delta T_b}{\Delta T_f} = \frac{T_b^2 \times l_f}{T_f^2 \times l_v}$ $T_b = 100 + 273 = 373 \text{ K}$ $T_f = 273 \text{ K}$ $\Delta T_b = 100.1 - 100$ = 0.1 °C $\frac{0.1}{\Delta T_f} = \frac{(373)^2 \times 80}{(273)^2 \times 540}$ $\Delta T_f = 0.36 \text{ °C}$ $T_f = -0.36 \text{ °C}$

EXAMPLE 2.27

The $K_{\rm sp}$ (25°C) of sparingly soluble salt XY₂(s) is 3.56×10^{-5} (mol L⁻¹)³ and at 30°C, the vapour pressure of its saturated solution in water is 31.78 mm of Hg. Calculate the enthalpy change of the reaction

$$XY_2(s) \rightleftharpoons X^{2+}(aq) + 2Y(aq)$$

Given: Vapour pressure of pure water = 31.82 mm of Hg

Sol. Let the solubility $XY_2(s)$ at 30°C be s mol L⁻¹.

$$XY_2(s) \rightleftharpoons X^{2+}(aq) + 2Y^{\odot}(aq)$$

$$\frac{P^{\circ} - P_{S}}{P_{S}} = \frac{n}{N}$$
 (i = 3, if 100% ionization)

$$\frac{31.82 - 31.78}{31.78} = 3\chi_2, \chi_2 = 0.0004, \frac{n_2}{n_1} = 0.004$$

$$n_2 = 55.6 \times 0.004 = 0.0233$$

$$S = 0.2333 \text{ mol } L^{-1}$$

$$K_{\rm sp}({\rm at~30^{\circ}C}) = (0.0233)(2 \times 0.0233)^{2}$$

= $5.05 \times 10^{-5}~({\rm mol~L^{-1}})^{3}$

$$K_{\rm sp}({\rm at~25^{\circ}C}) = 3.56 \times 10^{-5} ({\rm mol~L^{-1}})^{3}$$

Now,
$$\log \frac{K_{\rm sp}(35^{\circ}\text{C})}{K_{\rm sp}(25^{\circ}\text{C})} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\left(\frac{5.05\times10^{-5}}{3.56\times10^{-5}}\right) = \frac{\Delta H}{2.303\times8.314} \left(\frac{5}{303\times298}\right)$$

$$\Delta H = 52.5 \text{ kJ mol}^{-1}$$

Abnormal Molar Masses, Van't Hoff Factor

EXAMPLE 2.28

0.5 g KCl was dissolved in 100 g water, and the solution, originally at 20°C froze at -0.24°C. Calculate the percentage ionization of salt. $K_{\rm f}$ per 1000 g of water = 1.86°C.

Sol. Calculate the (theoretical) molecular mass of KCl

$$= 39 + 35.5 = 74.5$$

$$\Delta T_{\rm f} = iK_{\rm f} \cdot m$$

$$0.24 = i \times \frac{1.86 \times 0.5}{74.5 \times 100} \times 1000$$

$$i = 1.92$$

Now, KCl dissociates as KCl \rightleftharpoons K $^{\oplus}$ + Cl $^{\odot}$ Initial moles 1 0 0 Moles after dissociation 1 - α α

Total number of moles after dissociation

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

$$\therefore i = \frac{1+\alpha}{1}$$

or
$$\alpha = i - 1 = 1.92 - 1 = 0.92$$

Percentage ionization = $0.92 \times 100 = 92\%$

EXAMPLE 2.29

A 0.001 molal solution of a complex represented as $Pt(NH_3)_4Cl_4$ in water had freezing point depression of 0.0054°C. Given K_f for $H_2O=1.86~K~m^{-1}$. Assuming 100% ionization of the complex, write the ionization nature and formula of complex.

Sol. Let *n* atoms of Cl be acting as ligand. Then formula of complex and its ionization is:

Thus, particles after dissociation = 4 - n + 1 = 5 - nand therefore, Van't Hoff factor (i) = 5 - n

Now, $\Delta T_f = K'_f \times \text{Molality} \times \text{Van't Hoff factor}$

$$0.0054 = 1.86 \times 0.001 \times (5-n)$$

$$n = 2.1 \approx 2$$
 (integer value)

Thus, complex and its ionization is:

$$[\mathrm{Pt}(\mathrm{NH_3})_4\mathrm{Cl_2}]\mathrm{Cl_2} \rightarrow [\mathrm{Pt}(\mathrm{NH_3})_4\mathrm{Cl_2}]^{2+} + 2\mathrm{Cl}^{\odot}$$

EXAMPLE 2.30

Phenol associates in water to double molecules. The values of observed and calculated molecular weight of phenol are 161.84 and 94, respectively. The degree of association are 161.84 and 94 respectively. The degree of association of phenol will be

Sol.

b.
$$i = \frac{\text{Calculated molecular weight}}{\text{Observed molecular weight}} = \frac{94}{161.84} = 0.58$$

$$\alpha = \frac{1-i}{1-n} = \frac{1-0.58}{1-0.5} = \frac{0.42}{0.5}$$

$$\% \alpha = \frac{0.42}{0.5} \times 100 = 84\%$$

EXAMPLE 2.31

Calculate the Van't Hoff factor when $0.1 \text{ mol NH}_4\text{Cl is } \text{dissolved}$ in 1 L of water. The degree of dissociation of $\text{NH}_4\text{Cl is } 0.8 \text{ and}$ its degree of hydrolysis is 0.1.

Sol. Given,

Degree of dissociation (α) = 0.8

Degree of hydrolysis (h) = 0.1

Considering, ionization of NH₄Cl

Considering hydrolysis of NH₄[⊕] ion.

$$i = \frac{\text{Total moles at equilibrium}}{\text{Initial moles}}$$

$$0.2C + 0.8C + 0.8C + 0.8C(1 - h) + 0.8Ch + 0.08 Ch$$

$$\therefore i = \frac{C}{C}$$

$$= 2.68$$

EXAMPLE 2.32

0.5 m solution of acetic acid (Mw = 60) in benzene (Mw = 78) boils at 80.80°C. The normal boiling point of benzene is 80.10°C and $\Delta_{\text{vap}}H = 30.775 \text{ kJ mol}^{-1}$. Calculate the percent of association of acetic acid in benzene.

Sol. Given,

 T_0 (boiling point of benzene) = 80.10°C = 353.1 K $\Delta_{\text{vap}}H = 30.775 \text{ kJ mol}^{-1}$

$$Mw_1$$
(benzene) = 78

$$K_{\rm b} = \frac{RT_0^2 M w_1}{1000 \, \Delta_{\rm vap} H} = \frac{8.314 \times (353.1)^2 \times 78}{1000 \times 30.775 \times 10^3} = 2.63$$

$$\Delta T_{\rm b} = iK_{\rm b}m \implies i = \frac{\Delta T_{\rm b}}{K_{\rm b}m} = \frac{0.70}{2.65 \times 0.5} = 0.532$$

Considering association of acetic acid

Initially 1
$$CH_3COOH \longrightarrow (CH_3COOH)_2$$

At equilibrium 1 $-\alpha$

Total number of moles =
$$1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$i = \frac{\text{Total number of moles}}{\text{Initial moles}} = 1 - \frac{\alpha}{2}$$

$$0.532 = 1 - \frac{\alpha}{2}$$

EE.S 319MAX3

Astorage battery contains a solution of H₂SO₄ 38% by weight. Astorage Astorage Concentration, the Van't Hoff factor is 2.50. At what At una temperature will the battery contents freeze? $(K_f = 1.86^{\circ} \text{ mol}^{-1} \text{ kg})$

Given,
$$W_2 = 38 \text{ g}$$
, $W_{\text{H}_2\text{O}} = 100 - 38 = 62 \text{ g}$

$$\Delta T = \frac{1000 \times K_{\rm f} \times W_2}{Mw_2 \times W_1}$$

$$\Delta T = \frac{1000 \times 1.86 \times 38}{98 \times 62} \implies \Delta T_{\text{normal}} = 11.633$$

Now,
$$\frac{\Delta T_{\text{exp}}}{\Delta T_{\text{N}}} = i = 2.50$$

$$\Delta T_{\text{exp}} = 11.633 \times 2.50 = 29.08$$

Freezing point = 273 - 29.08 = 243.92 K

EXAMPLE 2.34

The freezing point of solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene.

$$(K_{\rm f} = 5.12 \text{ K mol}^{-1} \text{ kg}^{-1})$$



Sol.
$$\Delta T_f = iK_f m$$
, $0.45 = i \times 5.12 \times \frac{0.2 \times 1000}{60 \times 20}$

$$i = 0.527$$

$$2(CH_3COOH) \rightleftharpoons (CH_3COOH)_2$$

$$i = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

$$0.527 = 1 - \frac{\alpha}{2} \Rightarrow \alpha = 0.946$$

EXAMPLE 2.35

The degree of dissociation for PtCl₄ complex is 70%. Calculate the Van't Hoff factor.



$$PtCl_4 \iff Pt^{4+} + 4Cl^{\odot}$$

$$\frac{1}{1-\alpha}$$

Total moles =
$$1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$$

$$i = \frac{\text{Total moles at equilibrium}}{\text{Initial moles}} = \frac{1 + 4\alpha}{1} (\alpha = 70\% = 0.7)$$

$$i = 1 + 4 \times 0.7 = 3.8$$

Alternative method

$$i = \text{Number of ions} \times \alpha + (1 - \alpha)$$

$$= 5 \times 0.7 + (1 - 0.7)$$

$$=3.5+0.3=3.8$$

EXAMPLE 2.36

The degree of dissociation for K₄[Fe(CN)₆] is 60%. Calculate the Van't Hoff factor.

Sol.
$$K_4[Fe(CN)_6] \rightleftharpoons 4K^{\oplus} + [Fe(CN)_6]^{4}$$

Initial moles

Moles at equilibrium
$$1-\alpha$$

Total moles = $1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$

$$i = \frac{\text{Total moles at equilibrium}}{\text{Initial moles}} = \frac{1 + 4\alpha}{1}$$

$$= \frac{1 + 100}{1} \qquad (\alpha = 0.6)$$
$$= 1 + 4 \times 0.6 = 3.4$$

Alternative method

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= (5. \times 0.6) + (1-0.6)$$

$$= 3.0 + 0.4 = 3.4$$

EXAMPLE 2.37

The degree of association is 70% for the following reaction 2A (A)₂. Calculate the Van't Hoff factor.

Sol.

Initial moles Moles at equilibrium

Total moles =
$$1 - \alpha + \frac{\alpha}{2}$$

$$i = \frac{\text{Total moles at equilibrium}}{\text{Initial moles}} = 1 - \alpha + \frac{\alpha}{2}$$

$$= 1 - 0.7 + \frac{0.7}{2}$$

$$= 0.3 + 0.35 = 0.65$$

Alternative method

$$i = (\text{Number of ions} \times \alpha) + (1 - \alpha)$$

$$= \left(\frac{1}{2} \times 0.7\right) + (1 - 0.7)$$

= 0.35 + 0.3 = 0.65

EXAMPLE 2.38

Which of the following solutions in H₂O will show maximum depression in freezing point?

- a. 0.1 M K₂[HgI₄]
- **b.** 0.2 M Ba(NO₃),
- c. 0.3 M glucose
- d. 0.4 M NaCl
- Sol. d. Depression in freezing point ∞ Number of moles Therefore, greater the number of moles greater will be depression in freezing point.
 - **a.** For 0.1 M $K_2[HgI_4]$, i = 3.
 - No. of moles = $0.1 \times 3 = 0.3$
 - **b.** For 0.2 M Ba(NO₃)₂, i = 3
 - No. of moles = $0.2 \times 3 = 0.6$
 - c. For 0.3 M glucose, i = 1, (Non ionisable),

No. of moles =
$$0.3 \times 1 = 0.3$$

d. For 0.4 M NaCl, i = 2,

No. of moles = $0.4 \times 2 = 0.8$

Hence (d) is correct options.

EXAMPLE 2.39

Elevation in boiling point studies of $Ca(NO_3)_2$ gives molar mass as 131.2. The degree of dissociation of $Ca(NO_3)_2$ is

Sol. d.
$$Ca(NO_3)_2 \longrightarrow Ca^{2+} + 2NO_3^{\odot}$$
Initial 1 0 0
At eq 1-\alpha \alpha \alpha 2\alpha
 $i = 1 + 2\alpha$

Calculated Mw of $Ca(NO_3)_2 = 164$ Observed Mw of $Ca(NO_3)_2 = 131.2$

$$\therefore i = \frac{164}{131.2} = 1 + 2\alpha$$

$$\alpha = 0.125 = 12.5\%$$

EXAMPLE 2.40

Phenol associates in benzene to certain extent to form a dimer. A solution containing 20×10^{-3} kg of phenol in 1.0 kg of benzene has its freezing point depressed by 0.69 K. Calculate the fraction of phenol that has dimerized.

(K_f for benzene is 5.12 K kg mol-1).

Sol.

$$\begin{array}{l}
2C_{6}H_{5}OH & \Longrightarrow \\
1 \text{ mole} & 0 \\
1-\alpha & \alpha/2
\end{array}$$

$$\begin{aligned}
Total &= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \\
i &= \frac{1 - (\alpha/2)}{1} = 1 - \frac{\alpha}{2} \\
\Delta T_{f} &= iK_{f} \frac{W_{2} \times 1000}{Mw_{2} \times W_{1}} \\
0.69 &= \frac{i \times 5.12 \times 20 \times 10^{-3} \times 1000}{94 \times 1.0 \text{ kg}} \text{ kg} \\
i &= 0.633 \\
i &= 1 - \frac{\alpha}{2}, \ \alpha = 0.733 = 73.3\%
\end{aligned}$$

EXAMPLE 2.41

 $3 \, \mathrm{g}$ of urea and $9 \, \mathrm{g}$ of another non-volatile electrolytic compound (XY_2) were dissolved in 1000 g of water. The degree of dissociation of XY_2 is 0.5. The solution has a vapour pressure of 328.515 mm. Find the vapour density of XY_2 . The vapour pressure of water is 330 mm.

Sol.

Total moles =
$$1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

 $i = \frac{1+2\alpha}{1} = 1 + 2 \times 0.5 = 2$
 $n_{\text{H}_2\text{O}}(n_1) = \frac{1000}{18} = 55.55$; $n_{\text{urea}}(n_2) = \frac{3}{60} = 0.05$
 $n_{XY_2}(n_3) = \frac{9}{Mw_3}$
 $\chi_{\text{urea}} = \chi_2 = \frac{n_2}{n_1 + n_2 + n_3} = \frac{0.05}{55.55 + 0.05 + 9/Mw_3}$
 $= \frac{0.05}{55.6 + 9/Mw_3}$
 $\chi_{XY_2} = \chi_3 = \frac{9/Mw_3}{55.6 + 9/Mw_3}$
 $\frac{P^\circ - P_S}{P^\circ} = \chi_2 + i\chi_3$
 $\frac{330 - 328.515}{330} = \frac{0.05}{55.6 + 9/Mw_3} + 2 \times \frac{9/Mw_3}{55.6 + 9/Mw_3}$
 $0.0045 = \frac{1}{55.6 + 9/Mw_3} \left(0.05 + \frac{2 \times 9}{Mw_3}\right)$
Solve, $Mw_3 = 89.6$
 $VD = \frac{89.6}{2} = 44.8$

CONCEPT APPLICATION EXERCISE 2.4

- 1. Two liquids A and B form an ideal solution. If the mole fraction of A is χ at room temperature, the vapour pressure of solution is 85 mm. On the other hand if the mole fraction of B is χ at room temperature, the vapour pressure of solution is 95 mm. If $P_A^{\circ}/P_B^{\circ} = 1.25$, and the pressure over the mixture composed of 2 mol of A and 3 mol of at room temperature is reduced, at what pressure will be first trace of vapour form and what will be its composition
- 2. The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If $X_A = Y_A$ are the mole fractions of A in the liquid and vapor respectively find the value of X_A for which $Y_A I_A$ has a minimum. What is the value of pressure at the composition?
- 3. Dry air was successively passed through a solution of standard solute in 80 g water and then through pure water. The solution was 2.5 g and that of pure water was 0.04 g. What is the molecular weight of solute?
- 4. Two beaker A and B present in a closed vessel. Beaker A contains 152.4 g aqueous solution of urea, containing 12 g of urea. Beaker B contains 196.2 g glucose solution containing 18 g of glucose. Both solutions are allowed attain the equilibrium. Determine mass % of glucose in solution at equilibrium:
- 5. At 48°C, the vapour pressure of pure CS₂ is 850 tor. A solution of 2.0 g of sulphur in 100 g of CS₂ has a pressure 844.9 torr. Determine the atomicity of sulphur molecule:

- 6. An ideal solution contains two volatic liquids A ($P^{\circ} = 100$ $\frac{1}{2}$ while of B then total vapour pressure of the distillate $_{\text{(orr)}}^{\text{pur}}$ and B (P° = 200 torr). If mixture contain 1 mole of A
- The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 torr respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when I mole of mixture has been vaporized?
 - and 12% MgSO₄ by mass in solution. If % ionisation of Na,PO₄ and MgSO₄ are 50 amd 60 respectively then its $A_{\rm II}$ industrial waste water is found to contain $8.2\%~{\rm Na_3PO_4}$ normal boiling point is $[K_b(H_2O) = 0.50 \text{ K kg mol}^{-1}]$
- in their respective, solution $(AB_2 \text{ and } A_2B \text{ both are non-}$ electrolytes) is I mol/kg in both cases. Hence, atomic wt 9. Ratio of $\frac{\Delta I_b}{r}$ of $10\,\mathrm{g}\,AB_2$ and $14\,\mathrm{g}\,A_2B$ per $100\,\mathrm{g}$ of solvent of A and B are respectively:
- what is its freezing point? Given, enthalpy of fusion 10. If boiling point of an aqueous solutionsis 100.1°C, and vaporisation of water are 80 cal g⁻¹ and 540 cal g⁻¹ respectively.
- $0.1 M \mathrm{KI}$ and $0.2 M \mathrm{AgNO}_3$ are mixed in 3:1 volume ratio. The depression of freezing point of the resulting solution will be $[K_f(H_2O = 1.86 \text{ K kg mol}^{-1}]$:
 - $17.0\,\mathrm{tor}$ at this temperature, Applying Henry's and Raoult's laws, calculate the total vapour pressure for a 5 mole % at 293 K is 50.0 torr. The vapour pressure of pure water is The total pressure of a 4 mole % solution of NH_3 in water
- an ideal solution are 500 and 800 torr respectively at 300 \mathbb{R} A liquid solution of \mathcal{A} and \mathcal{B} for which the mole fraction of 4 is 0.06 is contained in a cylinder closed by a piston on The total pressure of two pure liquids A and B which form

which the pressure can be varried. The solution is slowly vaporized at 300 K by decreasing the applied pressure.

The composition of vapour when first bubble formed is:

- 14. Refer to Q. 13 above. What is the composition of last droplet of liquid remaining in equilibrium with vapour?
- 3.56×10^{-5} (mol L⁻¹)³ and at 30°C, the vapour pressure of 15. The $K_{\rm sp}$ (25°C) of sparingly soluble salt XY₂(s) is its saturated solution in water is 31.78 mm of Hg. Calculate the enthalpy change of the reaction

$$XY_2(s) \rightleftharpoons X^{2+}(aq) + 2Y^{\odot}(aq)$$

Given: Vapour pressure of pure water = 31.82 mm of Hg

- dimer. A solution containing 20×10^{-3} kg of phenol in 0.69 K. Calculate the fraction of phenol that has dimerized. 16. Phenol associates in benzene to certain extent to form a 1.0 kg of benzene has its freezing point depressed by $(K_{\rm f}$ for benzene is 5.12 K kg mol⁻¹).
- degree of dissociation of XY₂ is 0.5. The solution has a vapour pressure of 328.515 mm. Find the vapour density 17. 3 g of urea and 9 g of another non-volatile electrolytic compound (XY_2) were dissolved in 1000 g of water. The of XY_2 . The vapour pressure of water is 330 mm.

ANSWERS

- 1. P = 88 mm
- 4. Wt% of glucose = 14.49
 - **6.** $P_{\text{Total}} = 188.88 \text{ torr}$
 - 8. $T_b = 101.785$ °C
 - 10. $T_f = -0.361$ °C
- 12. $P_{\text{Total}} = 58.25 \text{ torr}$
- **14.** $x_A = 0.70, x_B = 0.30$ **16.** $\alpha = 0.733$
- 5. Atomicity of sulphur = 8

3. MW = 70.31

- 7. P = 300 torr
 - $9. M_A = 60, M_B = 20$
 - 11. $\Delta T_f = 0.279 \text{ K}$
- **13.** $y_A = 0.48, y_B = 0.52$ 15. $\Delta H = 52.5 \text{ kJ mol}^{-1}$
 - 17. V.D = 44.8

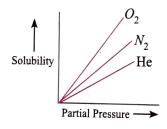
Exercises



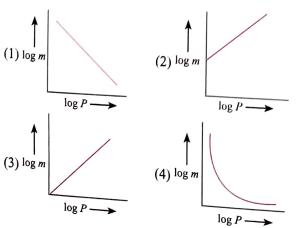
Single Correct Answer Type

Henry's Law

- 1. At same temperature, oxygen is more soluble in water than hydrogen. Which of them will have a higher value of K_H ?
 - (1) Oxygen
- (2) Hydrogen
- (3) Both have equal value (4) Can't predict
- 2. Henry's law is valid only when:
 - (1) Pressure is low
 - (2) Temperature is low
 - (3) The gas is not highly soluble
 - (4) The gas neither reacts chemically with solvent nor dissociates or associates in the solvent.
- 3. Air contins O₂ and N₂ in the ratio of 1:4. Calculate the ratio of solubilities in terms of mole fractions of N2 and O, dissolved in water at atmospheric pressure and at room temperature at which Henry's constant for O₂ and N₂ are 3.30×10^7 and 6.60×10^7 torr respectively.
 - (1) 1 : 2
- (2) 2 : 1
- (3) 3:1
- (4) 1:3
- 4. Molar solubility of helium, nitrogen and oxygen are plotted against partial pressure of the gas at constant temperature. Henry's law constant for these gases will lie in following sequence?



- $(1) O_2 > N_2 > He$
- $(2) O_2 < N_2 < He$
- (3) $O_2 = N_2 = He$
- $(4) O_2 > N_2 < He$
- 5. According to William Henry's the solubility of a gas in liquid depends on the pressure of the gas. If 'm' is the molality of the gas and 'P' is its pressire, then which of the following plot is in accordance with the law?



- Which of the following units is useful in relating concentration of solution with its vapour pressure?
 - (1) Mole fraction
- (2) Parts per million
- (3) Mass percentage
- (4) Molality
- 7. A sample of water is contamniated with 30 ppm of arsenic (As). The molality of As in water is (Aw of As = $75.0 \, \text{g}$)
 - (1) 2×10^{-2}
- (2) 4×10^{-2}
- $(3) 2 \times 10^{-3}$
- $(4) 4 \times 10^{-3}$
- 8. K_H (Henry's law constant) for CO₂ in water at 25°C is 3.0×10^{-2} mol L⁻¹ atm⁻¹. What is the concentration of C_0 in soft drink that is bottled with a partial pressure of Co of 5 atm. over the liquid at 25°C
 - (1) 0.15 M
- (2) 0.015 M
- (3) 0.30 M
- (4) 0.03 M

Raoult's Law, Ideal and Non-Ideal Solution, Azeotrope

- 9. 0.2 mole of liquid A is dissolved in 4.0 mole of H₂O. Total pressure of solution is 0.210 bar at 37°C. The vapour pressure of pure liquid (vapour pressure of water at 37°C= 0.198 bar) in bar is
 - (1) 0.448

- (2) 44.8
- (3) 0.224

- (4) 2.24
- 10. Two liquids A and B form an ideal solution. The vapour pressure of pure A and pure B are 66 mm Hg and 88 mm Hg, respectively. Calculate the composition of vapour Am the solution which is equilibrium and whose molar volume is 36%.
 - (1) 0.43

(2) 0.70

(3) 0.30

- (4) 0.50
- 11. At 27°C. the vapour pressure of an ideal solution containing 1 mole of A and 1 mole of B is 500 mm of Hg. At the same temperature, if 2 mol of B is added to this solution the vapout pressure of solution increases by 50 mm of Hg. The vapour pressure of A and B in their pure states is respectively.
 - (1) 600 mm, 400 mm
- (2) 400 mm, 600 mm
- (3) 300 mm, 700 mm
- (4) 200 mm, 800 mm
- 12. Mixture of volatile components A and B has total vapour pressure (in torr): $P_{\text{total}} = 254 - 119\chi_{\text{A}}$ where χ_A is the mole fraction of A in mixture. Hence p_A
 - and $p_{\rm B}^{\circ}$ are (in torr): (1) 254, 119
- (2) 119, 254
- (3) 135, 254
- (4) 154, 119
- 13. Negative deviations from Raoult's law are exhibited by binary mixtures
 - (1) in which the molecules tend to attract each other and hence their escape into the vapour phase is retarded.
 - (2) in which the molecules tend to repel each other and hence their escape into the vapour phase is retarded.
 - (3) in which the molecules tend to attract each other and hence their escape into the vapour phase is speeded up

14. Mole fraction of component A in vapour phase is χ_1 and mole fraction of component A in liquid mixture is $\chi_2(p_A^\circ)$ = vapour pressure of pure A), then the total vapour pressure of the liquid mixture is

(1) $\frac{p_A^{\circ}\chi_2}{\chi_1}$ (3) $\frac{p_B^{\circ}\chi_1}{\chi_2}$

(2) $\frac{p_{A}^{\circ}\chi_{1}}{\chi_{2}}$ (4) $\frac{p_{B}^{\circ}\chi_{2}}{\chi_{2}}$

15. At 25°C, the vapour pressure of pure methyl alcohol is 92.0 tort. Mol fraction of CH₃OH in a solution in which vapour pressure of CH₃OH is 23.0 torr at 25°C, is:

(1) 0.25

(2) 0.75

(3) 0.50

(4) 0.66

16. The vapour pressure of pure benzene C₆H₆ at 50°C is 268 torr. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure of 167 torr at 50°C?

(1) 0.377

(2) 0.605

(3) 0.623

(4) 0.395

17. The vapour pressure of pure liquid solvent A is 0.80 atm. When a non-volatile substance B is added to the solvent, its vapour pressure drops to 0.60 atm; the mole fraction of component B in the solution is

(1) 0

(2) 0.25

(3) 2.0

(4) 3.0

18. The vapour pressure of a pure liquid A is 40 mm Hg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mm Hg. The mole fraction of A in the solution, if it obeys Raoult's law, is:

(1) 0.8

(2) 0.5

(3) 0.2

(4) 0.4

19. The boiling point of an azeotropic mixture of water and ethyl alcohol is less than that of the theoretical value of water and alcohol mixture. Hence the mixture shows

- (1) The solution is highly saturated.
- (2) Positive deviation from Raoult's law.
- (3) Negative deviation from Raoult's law.
- (4) Nothing can be said.

20. Solution distilled without change in composition at a temperature is called

(1) Amorphous

(2) Azeotropic mixture

(3) Ideal solution

(4) Super saturated solution

21. Azeotropic mixtures are

- (1) Constant boiling point mixture without changing the composition.
- (2) Those which boil at different temperatures.
- (3) Mixtures of two solids.
- (4) None of the above

22. On mixing 10 mL of acetone with 40 mL of chloroform, the total volume of the solution is

(1) < 50 mL

(2) > 50 mL

(3) = 50 mL

(4) Cannot be predicted

23. Which of the following substances will lose its solubility with increase in temperature?

(1) NaOH

(2) Na_2CO_3 (3) Na_2SO_4 (4) All

24. On mixing 10 mL of carbon tetrachloride with 10 mL of benzene, the total volume of the solution is

(1) > 20 mL

(2) < 20 mL

(3) = 20 mL

(4) Cannot be predicted

25. If Raoult's law is obeyed, the vapour pressure of the solvent in a solution is directly proportional to

- (1) The mole fraction of the solvent.
- (2) The mole fraction of the solute.
- (3) The mole fraction of the solvent and solute.
- (4) The volume of the solution.

26. Each pair forms ideal solution except

(1) C_2H_5Br and C_2H_5I

(2) C₆H₅Cl and C₆H₅Br

(3) C_6H_6 and C_6H_5 · CH_3

(4) C₂H₅I and C₂H₅OH

27. An aqueous solution of methanol in water has vapour pressure

- (1) Equal to that of water
- (2) Equal to that of methanol
- (3) More than that of water
- (4) Less than that of water

28. Which condition is not satisfied by an ideal solution?

- $(1) \Delta_{\min} H = 0$
- (2) $\Delta_{\text{mix}}V = 0$
- $(3) \Delta_{\min} S = 0$
- (4) Obeyance of Raoult's law

29. A mixture of benzene and toluene forms

(1) An ideal solution

(2) Non-ideal solution

(3) Suspension

(4) Emulsion

30. A pressure cooker reduces cooking time because

- (1) Heat is more evenly distributed
- (2) Boiling point of water inside the cooker is increased
- (3) The high pressure tenderizes the food
- (4) All of these

31. If P° and P_{\circ} are vapour pressures of solvent and its solution, respectively, χ_1 and χ_2 are mole fractions of solvent and solute, respectively, then

$$(1) P_s = P^o/\chi_2$$

$$(2) P^{o} - P_{s} = P^{o} \chi_{2}$$

$$(3) P_{\rm s} = P^{\rm o} \chi_2$$

(3)
$$P_s = P^s \chi_2$$

(4) $\frac{P^o - P_s}{P_s} = \frac{\chi_1}{\chi_1 + \chi_2}$

32. Dry air was passed successively through a solution of 5 g of a solute in 180 g of water and then through pure water. The loss in the weight of solution was 2.50 g and that of pure solvent 0.04 g. The molecular weight of the solute is

- (1) 31.25
- (2) 3.125
- (3) 312.5
- (4) None
- 33. At 40°C, the vapour pressures of pure liquids, benzene, and toluene, are 160 mm Hg and 60 mm Hg, respectively. At the same temperature, the vapour pressure of an equimolar solution of the two liquids, assuming the ideal solution, should be
 - (1) 140 mm Hg
- (2) 110 mm Hg
- (3) 220 mm Hg
- (4) 100 mm Hg
- 34. An azeotropic mixture of HCl and water has
 - (1) 84% of HCl
- (2) 22.2% HCl
- (3) 63% of HCl
- (4) 20.2% HCl
- 35. An ideal solution was obtained by mixing methanol and ethanol. If the partial vapour pressure of methanol and ethanol are 2.619 kPa and 4.556 kPa, respectively, the composition of vapour (in terms of mole fraction) will be
 - (1) 0.635 MeOH, 0.365 EtOH
 - (2) 0.365 MeOH, 0.635 EtOH
 - (3) 0.574 MeOH, 0.326 EtOH
 - (4) 0.173 MeOH, 0.827 EtOH
- 36. The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be the mole fraction of solvent if the decrease in vapour pressure is 20 mm of Hg.
 - (1) 0.8
- (2) 0.6
- (3) 0.4
- (4) 0.2
- 37. The mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene ($P_B^{\circ} = 120 \text{ torr}$) and toluene ($P_T^{\circ} = 80 \text{ torr}$) having 2.0 mol of each, is
 - (1) 0.50
- (2) 0.25
- (3) 0.60
- (4) 0.40
- 38. The total vapour pressure of a mixture of 1 mol A $(P_A^{\circ} = 150 \text{ torr})$ and 2 mol B $(P_B^{\circ} = 240 \text{ torr})$ is 200 mm. In this case
 - (1) There is positive deviation from Raoult's law.
 - (2) There is negative deviation from Raoult's law.
 - (3) There is no deviation from Raoult's law.
 - (4) Molecular masses of A and B are also required.
- 39. The vapour pressure of pure benzene C_6H_6 at 50°C is 268 torr. How many moles of non-volatile solute per mole of benzene is required to prepare a solution of benzene having a vapour pressure of 167 torr at 50°C?
 - (1) 0.377
- (2) 0.605
- (3) 0.623
- (4) 0.395
- 40. The most likely of the following mixtures to be an ideal solution is
 - (1) NaCl—H₂O
- (2) $C_2H_5OH-C_6H_6$
- (3) $C_6H_{16}(I)$ — H_2O
- $(4) C_6 H_5 O H H_2 O$
- 41. The mole fraction of component A in vapour phase is χ_1 and mole fraction of component A in liquid mixture is χ_2 $(P_A^{\circ} = \text{vapour pressure of pure A}; P_B^{\circ} = \text{vapour pressure})$ of pure B). Then total vapour pressure of the liquid mixture is

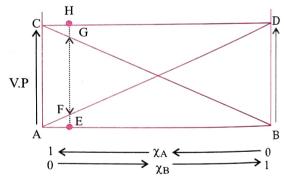
- $(1) \frac{P_{A}^{\circ}\chi_{2}}{\chi_{1}} \quad (2) \frac{P_{A}^{\circ}\chi_{1}}{\chi_{2}} \quad (3) \frac{P_{A}^{\circ}\chi_{1}}{\chi_{2}} \quad (4) \underbrace{P_{B}^{\circ}\chi_{2}}_{}$

- 42. The relative decrease in the vapour pressure of an aqueous solution containing 2 mol [Cu(NH₃)₃Cl]Cl in 3 mol H₂O₁k 0.50. On reaction with AgNO₃, this solution will form
 - (1) 1 mol AgCl
- (2) 0.25 mol AgCl
- (3) 2 mol AgCl
- (4) 0.40 mol AgCl
- 43. A mixture of volatile components A and B has total Vapolin pressure (in torr)

$$P = 254 - 119\chi_{A}$$

where χ_A is the mole fraction of A in mixture. Hence $P_{\rm A}^{\circ}$ and $P_{\rm B}^{\circ}$ are (in torr)

- (1) 254, 119 (2) 119, 254 (3) 135, 254 (4) 154, 119
- 44. Based on the given diagram, which of the following statements regarding the solutions of two miscible volatila liquids are correct?
 - 1. Plots AD and BC show that Raoult's law is obeyed for the solution in which B is a solvent and A is the solute and as well as for that in which A is solvent and B is solute
 - 2. Plot CD shows that Dalton's law of partial pressures in observed by the binary solutions of components A and R
 - 3. EF + EG = EH; and AC and BD corresponds to the vapour pressures of the pure solvents A and B, respectively.



Select the correct answer using the codes given below: Codes:

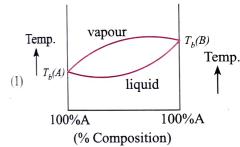
- (1) 1 and 2
- (2) 2 and 3
- (3) 1 and 3
- (4) 1, 2, and 3
- 45. Which of the following graph represent the behavior of ideal binary liquid mixture?
 - (1) Plot of $1/P_{\text{Total}}$ against x_A is linear
 - (2) Plot of $1/P_{\text{Total}}$ against x_{B} is linear
 - (3) Plot of P_{Total} against x_A is linear
 - (4) Plot of P_{Total} against x_{B} is linear

(Here x_A and x_B are the mole fraction of components A^{appl} B in vapour phase) B in vapour phase)

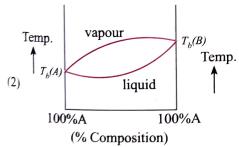
- 46. A maxima of minima obtained in the temperalures composition curve of a mixture of two liquids indicates:
 - (1) An azeotropic mixture

- (2) An eutectic formation
- (3) That the liquids are immoscible with one another
- (4) that the liquids are partially miscible at the maximum or minimum
- A solution has 1: 4 mole ratio of pentane to hexane.

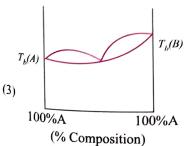
 The vapour pressure of pure hydrocarbons at 20°C are 440 mm Hg for pentane and 120 mm Hg for hexane. The mole fraction of pentane in vapour phase would be:
 - (1) 0.786
 - (2) 0.549
 - (3) 0.478
 - (4) 0.200
- 18. The lubricating action of an oil is more if it possess:
 - (1) High vapour pressure
 - (2) Low vapour pressure
 - (3) High surface tension
 - (4) High density
- 49. When a plot of boiling point versus composition is plotted, then type of graph than can be obtained is:



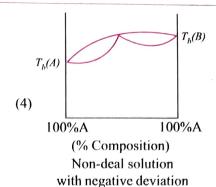
For ideal solution with $P_A^0 > P_B^0$



For ideal solution with $P_A^0 < P_B^0$



Non-deal solution
with positive deviation

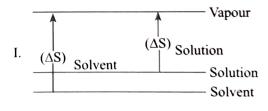


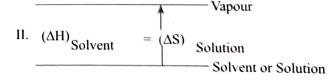
- **50.** An ideal solution has two components A and B. If A is more volatile than B and also $P_A^0 > P_T$, then the correct relation between mole fraction of A in liquid (X) and vapour (Y) phase is:
 - $(1) X_{\mathsf{A}} = Y_{\mathsf{A}}$
- $(2) X_{\mathsf{A}} > Y_{\mathsf{A}}$
- $(3) X_{\mathsf{A}} < Y_{\mathsf{A}}$
- (4) Can't be predicted
- 51. The normal boiling point of water is 373 K, Vapour pressure of water at temperature T is 19 mm Hg. If enthalpy of vaporisation is 40.67 kJ/mol, then temperature T would be (Use: $\log 2 = 0.3$, R: 8.3 JK⁻¹ mol⁻¹):
 - (1) 250 K
- (2) 291.4 K
- (3) 230 K
- (4) 290 K
- **52.** Two liquids A and B have P_A° and P_B° in the ratio of 1:3 and the ratio of number of moles A and B in liquid phase are 1:3. Then mole fraction of 'A' in vapour phase in equilibrium with the solution is equal to"
 - (1) 0.1

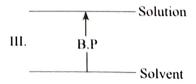
(2) 0.2

(3) 0.5

- (4) 1.0
- **53.** Which represents correct difference when non-volatile solute is present in an ideal solution?



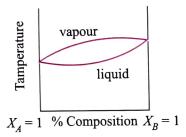




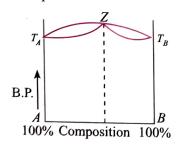
- (1) I, II, III
- (2) I, III
- (3) II, III
- (4) I, II

54. Select correct statement?

- (1) Heat of vaporisation for a pure solvent and for a solution are similar because similar intermolecular forces between solvent molecules must be overcome in both cases
- (2) Entropy change between solution and vapour is smaller than the entropy change between pure solvent and vapour
- (3) Boiling point of the solution is larger than that of the pure solvent
- (4) All are correct statements
- 55. Boiling point composition diagram of the liquid-vapour equilibrium for A and B is shown in the figure. If a binary liquid mixture of A and B is distilled fractionally, which of the following would be correct observation?



- (1) Composition of the stll (residue) will approach pure liquid B only
- (2) COmposition of the distillate will approach pure A only
- (3) Composition of distillate and residue will approach pure A and B respectively
- (4) Neither of the component can be obtained in pure state
- 56. A liquid mixture having composition corresponding to point Z in the figure shown is subjected to distillation at constant pressure. Which of the following statement is correct about the process?



- (1) The composition of distillate differs from the mixture
- (2) The boiling point goes on changing
- (3) The mixture has highest vapour pressure than for any other composition
- (4) Composition of an azeotrope alters on changing the external pressure
- 57. Which will form maximum boiling azeotrope?
 - (1) $C_6H_6 + C_6H_5CH_3$ solution
 - (2) HNO₃ + H₂O solution

- (3) $C_2H_5OH + H_2O$ solution
- (4) n-hexane and n-heptane
- 58. Total vapour pressure of mixture 1 mole of Volatile component A ($P_A^{\circ} = 100$ mm Hg) and 3 mole of V_0 component B ($P_B^{\circ} = 80$ mmHg) is 90 mm Hg. For such case:
 - (1) There is positive deviation from Raoult's law
 - (2) Boiling point has been lowered
 - (3) Force of attraction between A and B is weaker than that between A and A or between B and B
 - (4) All the above statements are correct
- **59.** Two components A and B form an ideal solution. The m_{0lo} fraction of A and B in ideal solution are X_A and X_B , while that of in vapour phase, these components have their mole fractions as Y_A and Y_B . Then, the slope and intercept of $p|_{01}$ of $\frac{1}{Y_A}vs.\frac{1}{X_A}$ will be:

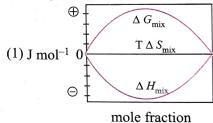
$$(1) \frac{P_A^{\circ}}{P_B^{\circ}}, \frac{P_B^{\circ} - P_A^{\circ}}{P_B^{\circ}}$$

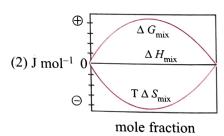
$$(2) \frac{P_B^{\circ}}{P_A^{\circ}}, \frac{P_A^{\circ} - P_B^{\circ}}{P_A^{\circ}}$$

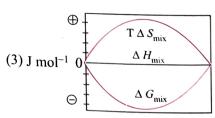
(3)
$$\frac{P_B^{\circ}}{P_A^{\circ}}, \frac{P_B^{\circ}}{P_B^{\circ} - P_A^{\circ}}$$
 (4) $P_A^{\circ} - P_B^{\circ}, \frac{P_A^{\circ}}{P_B^{\circ}}$

$$(4) P_A^{\circ} - P_B^{\circ}, \frac{P_A^{\circ}}{P_B^{\circ}}$$

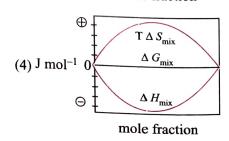
60. Which of the following represents correctly the changes in therodynamic properties during the formation of 1 mole of an ideal binary solution?







mole fraction



2.77

- 61. 100 g of C₆H₁₂O₆(aq) solution has vapour pressure is equal to 40 torr at certain temperature. Vapour pressure of equal to $H_2O(1)$ is 40.18 torr at same temperature. If this solution is H₂O(t) = 0.93°C, what mass of ice will be separeted out? $(K_f = 1.86 \text{ kg mol}^{-1})$
 - (1) 95.5 g

(2) 4.5 g

(3) 45.5 g

(4) 47.8 g

Colligative Properties and Vant Hoff Factor

62. An aqueous solution freezes at -2.55°C. What is its boiling $K_{b(H_2O)} = 0.52 \text{ K m}^{-1}; K_f^{H_2O} = 1.86 \text{ K m}^{-1}$? (1) 107.0°C (2) 100.6°C (3) 100.1°C

(4) 100.7°C

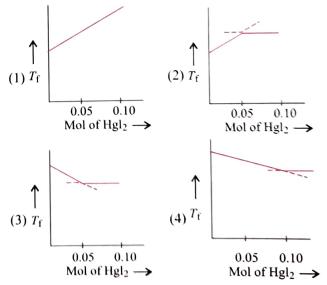
- 3. The relative decrease in VP of an aqueous glucose dilute solution is found to be 0.018. Hence, the elevation in boiling point is (it is given 1 molal aqueous urea solution boils at 100.54°C at 1 atm pressure)
 - $(1) 0.018^{\circ}$
- $(2) 0.18^{\circ}$
- $(3) 0.54^{\circ}$
- $(4) 0.03^{\circ}$
- 64. 10.0 g of glucose (π_1) , 10.0 g of urea (π_2) , and 10.0 g of sucrose (π_3) are dissolved in 250.0 mL of water at 273 K $(\pi = osmotic pressure of a solution)$. The relationship between the osmotic pressure of the solutions is
 - (1) $\pi_1 > \pi_2 > \pi_3$
- (2) $\pi_3 > \pi_1 > \pi_2$
- (3) $\pi_2 > \pi_1 > \pi_3$
- (4) $\pi_2 > \pi_3 > \pi_1$
- 65. 0.6 g of a solute is dissolved in 0.1 L of a solvent which develops an osmotic pressure of 1.23 atm at 27°C. The molecular weight of the solute is
 - (1) 149.5 g mol^{-1}
- (2) 120.0 g mol^{-1}
- $(3) 430.0 \text{ g mol}^{-1}$
- (4) None of these
- 66. A 5% solution of cane sugar (molecular weight = 342) is isotonic with a 1% solution of substance X. The molecular weight of X is
 - (1)342
- (2) 171.12
- (3)65.6
- (4) 136.8
- 67. What mass of urea be dissolved in 171 g of water so as to decrease the vapour pressure of water by 5%?
 - (1) 15 g
- (2) 20 g
- (3) 25 g
- $(4)\ 30\ g$
- 68. The vapour pressure at a given temperature of an ideal solution containing 0.2 mol of non-volatile solute and 0.8 mol of a solvent is 60 mm of Hg. The vapour pressure of the pure solvent at the same temperature will be
 - (1) 120 mm Hg
- (2) 150 mm Hg
- (3) 60 mm Hg
- (4) 75 mm Hg
- 69. The vapour pressure of a solution containing 5.0 g of a nonelectrolyte in 100.0 g of water at a particular temperature is 2985 N m⁻². If the vapour pressure of pure water is 3000 N m⁻², the molecular weight of the solute is
 - (1)60.0

- (2) 120.0
- (3) 180.0
- (4)380.0
- 70. The molal boiling point constant for water is 0.513 K m⁻¹. When 0.1 mole of sugar is dissolved in 200.0 g of water, the solution boils under a pressure 1.0 atm at
 - (1) 100.513°C
- (2) 100.0513°C
- (3) 100.256°C
- (4) 101.025°C

- 71. What should be the boiling point of 1.0 molal aqueous KCl solution (assuming complete dissociation of KCl) if $K_{b(H_2O)}$ is 0.52 K m⁻¹?
 - (1) 100.52°C
- (2) 101.04°C
- (3) 99.48°C
- (4) 98.96°C
- 72. The ratio of freezing point depression values of 0.01 M solutions of urea, common salt, and Na2SO4 are
 - (1) 1:1:1
- (2) 1:2:1
- (3) 1:2:3
- (4) 2:2:3
- 73. From a measurement of the freezing point depression of benzene, the molecular weight of acetic acid in a benzene solution was determined to be 100. The percentage association of acetic acid is
 - (1) 79%
- (2)93%
- (3) 80%
- (4) 100%
- 74. An aqueous solution containing an ionic salt having molality equal to 0.19 freezes at -0.704°C. The Van't Hoff factor of the ionic salt is $(K_f \text{ for water} = 1.86 \text{ K m}^{-1})$
 - (1)3
- (2)2
- (3)4
- (4)5
- 75. The Van't Hoff factor for a 0.1 M Al₂(SO₄)₃ solution is 4.20. The degree of dissociation is
 - (1)80%
- (2)90%
- (3)78%
- (4) 83%
- 76. The degree of dissociation α of a weak electrolyte is
 - $(1) \ \frac{i-1}{n+1}$
- $(2) \ \frac{i-1}{n-1}$
- (3) $\frac{n-1}{i-1}$
- $(4) \frac{n+1}{i-1}$

where n is the number of ions given by 1 mol of electrolyte.

77. Increasing amount of solid HgI2 is added to 1 L of an aqueous solution containing 0.1 mol KI. Which of the following graphs do represent the variation of freezing point of the resulting solution with the amount of HgI2 added?



- 78. Equimolal solutions of KCl and compound X in water show depression in freezing point in the ratio of 4:1. Assuming KCl to be completely ionized, the compound X in solution must
 - (1) Dissociate to the extent of 50%
 - (2) Hydrolyze to the extent of 80%
 - (3) Dimerize to the extent of 50%
 - (4) Trimerize to the extent of 75%

2.78	Physical Chemistry	72 (02)	88.	Which salt shows maxi	mum osmotic pressure in its h
79.	Arrange the following as d	irected: (Q.79–82)	001	SAIDHOHA	(0) (1)
	ncreasing order of boiling points. (1) $\Delta \sigma NO_{s}$ (2) $Na_{2}SO_{4}$ (3) (NH)		M_4 (3) $(NH_4)_3PO_4$ (4) M_{gC_1}		
	I. 0.001 m NaCl	II. 0.001 m urea	89.	Which solution will show	maximum occident modiling not
	III. 0.001 m MgCl ₂	IV. 0.001 m CH ₃ COOH		(1) 0.1 M KCI	(2) 0.1 M DaC ₁₂
	(1) $11 < IV < I < 111$	(2) II < I < IV < III		(3) 0. 1 MFeCl ₃	(4) 0.1M $\text{Fe}_2(\text{SO}_4)_3$
	(3) III < I < IV < II	(4) III < IV < I < II	90.	When common salt is d	issolved in water
80.	Increasing order freezing p	points.		(1) The melting point of	the solution increases.
	I. 0.1 M ethanol	II. $0.1 \text{ M Ba}_3(PO_4)_2$		(2) The boiling point of	solution decreases.
	III. $0.1 \text{ M Na}_2 \text{SO}_4$				and boiling point decrease.
	(1) II < III < I	(2) $11 < I < 111$		(4) The boiling point of	
	(3) 1 < III < II	(4) III < I < II	91.	A teacher one day poin	ted out to his students the peculiar
81.	Increasing order of osmoti	c pressure.		fact that water is a unic	que liquid which freezes exactly at
011	I. 0.1 M glucose	II. 1% urea solution		find the correct statemen	at 100°C. He asked the students to
	III. 0.1 M common salt				nything, however sparingly the
	(1) III < II < I	(2) III < I < II		dissolution may be.	in the sparingly the
	(3) I < II < III	(4) II < I < III		(2) Water is a polar mo	lecule.
0.5	. Increasing order of Van't I				g temperatures of water were used
82				to define a temperat	
	I. NaNO ₃	II. BaCl ₂		(4) Liquid water is den	ser than ice.
	III. $K_3[Fe(CN)_6]$	IV. $C_6H_{12}O_6$	92.	The osmotic pressure	of a dilute solution is directly
	V. CH ₃ COOH	(O) W H L H W.		proportional to the	
	$(1) \coprod < I < V < IV < \coprod$			(1) Diffusion rate of the	e solute
	$(3) \coprod < \coprod < I < V < IV$	(4) IV < V = I < II < III		(2) Ionic concentration	
83	. The use of common salts, is made to clear snow on the salts.	e.g., NaCl or CaCl ₂ anhydrous,		(3) Boiling point	
	(1) A lowering in the free			(4) Flow of solvent fro	m a concentrated solution
	(2) A lowering in the mel		93.		aqueous solution of calcium nitrate
		erature of atmosphere present at		will be	
	that time.	•		(1) 0°C	(2) Above 0°C
	(4) All of these.		0.4	(3) 1°C	(4) Below 0°C
84	_	apour pressure is equal to the mole e solute. This statement was given	94.	separate a solution from passage of	meable membrane when used 10 m its solvent permits through it the
	(1) Raoult (2) Henry	(3) Joule (4) Dalton		(1) Solute only	(2) Solvent only
8		e 90% dissociated which of the		(3) Both (1) and (2)	(4) None
	following will have the h	ighest osmotic pressure?	95	. Which statement is inc	correct about osmotic pressure (x)
	(1) Decinormal Al ₂ (SO ₄)	3		volume (V) , and tempe	rature (T)?
	(2) Decinormal BaCl ₂			(1) $\pi \propto \frac{1}{\nu}$, if T is cons	stant
	(3) Decinormal Na₂SO₄(4) A solution obtained	by mixing equal volumes of (2)		$(2) \pi \propto T, \text{ if } V \text{ is consta}$	
•	and (3) and filtering			(3) $\pi \propto V$, if T is constant	
ō	o. When a solution is sepa	trated from a solvent by a semi-		(4) πV is constant, if T	
	is called as	nen the phenomenon taking place	96	 Semi-permeable members 	orane is chemically
	(1) Osmosis (2) Diffusi	on (3) Solubility (4) None		Copper ferrocyanid	le
1	37. If a thin slice of sugar	beet is placed in concentrated		(2) Copper ferricyanid	e
	solution of NaCl, then			(3) Copper sulphate	
	(1) Sugar beet will lose	water from its cells.		(4) Potassium ferrocya	nide
	Sugar beet will absort	rb water from solution	97	 (4) Potassium ferrocyanide The depression in freezing point is maximum if the solvent used is 	
	(3) Sugar beet will neith	er absorb nor lose water.			
	(4) Sugar beet will disso	olve in solution.		(1) Camphor	(2) Naphthalene
				(3) Benzene	(4) Water

98. The osmotic pressure of a dilute solution is given by

 $(1) P = P_0 \times N_1$

 $(3) \Delta P = P_0 N_2$

$$(4) \frac{\Delta P}{P^{\circ}} = \frac{P^{\circ} - P_{\rm S}}{P^{\circ}}$$

Which is not a colligative property?

- (1) Lowering of vapour pressure
- (2) Freezing point
- (3) Osmotic pressure
- (4) Elevation in boiling point

100. Blood has been found to be isotonic with

- (1) Normal saline solution
- (2) Saturated NaCl solution
- (3) Saturated KCl solution
- (4) Saturated solution of a 1:1 mixture of NaCl and KCl

101. Isotonic solutions are those which have

- (1) Same osmotic pressure
- (2) Same molarity
- (3) Same density
- (4) Same normality

102. The correct relationship between the boiling points of very dilute solutions of AlCl₂ (t_1) and CaCl₂ (t_2) , having the same molar concentration, is

(1) $t_1 = t_2$

(2) $t_1 > t_2$

 $(3) t_2 > t_1$

 $(4) t_2 \ge t_1$

103. Two solutions of KNO₃ and CH₃COOH are prepared separately. The molarity of both is 0.1 M and osmotic pressure is P_1 and P_2 , respectively.

The correct relationship between the osmotic pressures is

 $(1) P_2 > P_1$

(2) $P_1 = P_2$

 $(3) P_1 > P_2$

(7.)

(4)
$$\frac{P_1}{P_1 + P_2} = \frac{P_2}{P_1 + P_2}$$

104. Boiling point elevation is

- (1) Additive property
- (2) Constitutive property
- (3) Colligative property
- (4) Partly additive and partly constitutive

105. An example of colligative property is

- (1) Freezing point
- (2) Boiling point
- (3) Vapour pressure
- (4) Osmotic pressure

106. The colligative properties of a solution depend on

- (1) The number of solute particles present in it
- (2) The chemical nature of the solute particles present in it
- (3) The nature of the solvent used
- (4) None of these
- 107. Osmosis is the spontaneous flow through a semi-permeable membrane of
 - (1) A less concentrated solution into more concentrated solution
 - (2) The solvent from a solution of lower concentration to one of higher concentration

- (3) Solute particles from a solution of higher concentration to one of lower concentration
- (4) None of these
- 108. The osmotic pressure of a non-aqueous solution is measured
 - (1) Berkeley and Hartley method
 - (2) Pfeffer's method
 - (3) Morse and Frazer method
 - (4) Townend's method
- 109. The osmotic pressure of a solution increases if
 - (1) Temperature is lowered
 - (2) Volume is increased
 - (3) Number of solute molecules is increased
 - (4) None of these
- 110. The ratio of the value of any colligative property for KCl solution to that of sugar solution is
 - (1) 1
- (2) 0.5
- (3)2

(4)4

- 111. Equimolal solutions A and B show depression in freezing point in the ratio 2:1. A remains in the normal state in solution. B will be
 - (1) Normal in solution
- (2) Dissociated in solution
- (3) Associated in solution (4) Hydrolysed in solution
- 112. The vapour pressure (VP) of a dilute solution of non-volatile solute is P and the VP of a pure solvent is P° . The lowering of the VP is
 - (1) +ve
- (2) –ve
- (3) P/P°
- (4) P°/P
- 113. The value of K_f for water is 1.86°, calculated from glucose solution. The value of $K_{\rm f}$ for water calculated for NaCl solution will be
 - (1) = 1.86
- (2) < 1.86
- (3) > 1.86
- (4) Zero
- 114. What will be the molecular weight of NaCl determined experimentally following elevation in the boiling point or depression in freezing point method?
 - (1) < 58.5
- (2) > 58.5
- (3) = 58.5
- (4) None
- 115. The Van't Hoff factor of NaCl assuming 100% dissociation (3) 1
 - (1) 1/2
- (2)2

- 116. The solutions in which the blood cells retain their normal shape, with regard to the blood, are
 - (1) Isotonic
- (2) Hypertonic
- (3) Hypotonic
- (4) None of these
- 117. The factor $\Delta T_f/K_f$ represents
 - (1) Molarity (2) Formality (3) Normality (4) Molality
- 118. Which of the following solutions has minimum freezing point?
 - (1) 0.01M NaCl
- (2) $0.005 \text{ M C}_2\text{H}_5\text{OH}$
- (3) 0.005 M Mgl₂
- $(4) 0.005 \text{ M MgSO}_{4}$
- 119. Which of the following solutions will have the highest boiling point?
 - (1) 1% glucose in water
- (2) 1% sucrose in water
- (3) 1% NaCl in water
- (4) 1% CaCl, in water

	Physical Chemistry	120	What would be the freez	ing point of aqueous solution
2.80	Physical Chemistry Which of the following solutions has the minimum freezing	130.	containing 1/ g or C2	H ₅ OH in 1000 g of Water
120.	Which of the following solutions		$K_{\rm f H_2 O} = 1.86 \text{ K m}^{-1}.$	•
	point? (1) 1 molal NaCl solution (2) 1 molal KCl solution (3) 1 molal urea solution		$^{\text{H}_{\text{f}}\text{H}_{2}\text{O}}$ (1) -0.69°C	(2) -0.34°C
	(2) 1 moles CaCl solution (4) I molar the			(4) 0.34°C
	The osmotic pressure of equimolar solutions of		(3) 0.0°C	` '
121.	BaCl ₂ , NaCl, and glucose follow the order	131.	A solution containing 6.6	g urea in 1 L was found to be
	BaCl ₂ , NaCl, and glacest standard and a standard a standard and		isotonic with a 5% (Weigh	t/volume) solution of an organic
	(1) BaCl ₂ > NaCl > Glucose		non-volatile solute. The m	(2) 2480 (4) 261
	(2) Glucose > NaCl > BaCl ₂		(1) 348.9 (2) 34.89	(3) 3489 (4) 861.2
	(3) NaCl > BaCl ₂ > Glucose	132.	A solution containing 4 g	of a non-volatile organic solute
	(4) NaCl > Glucose > BaCl ₂		ner 100 mL was found to h	ave an osmotic pressure equal to
122.	Which of the following solutions has the maximum freezing		500 cm of mercury at 27°C	. The molecular weight of solute
	point?		is	
	(1) 1 molar of NaCl solution		(1) 14.97 (2) 149.7	(3) 1697 (4) 1.497
	(2) 1 molar of KC1 solution	122	The molal elevation const	tant of water = 0.52 K m^{-1} . The
	(3) 1 molar of CaCl ₂ solution	133.	boiling point of 1.0 molal	aqueous KCl solution (assuming
	(4) 1 molar of urea solution		complete dissociation of k	(Cl) should be
123.	The osmotic pressure of a 5% (weight/volume) solution of		(1) 100.52°C	(2) 101.04°C
	cane sugar at 150°C is			(4) 98.96°C
	(1) 4 atm (2) 3.4 atm (3) 5.078 atm (4) 2.45 atm		(3) 99.48°C	
124.	The freezing point of a 0.05 molal solution of non-electrolyte	134.	If a 6.84% (weight/vol	ume) solution of cane suga
	in water is		(molecular weight = 342)	is isotonic with 1.52% (weight
	$(K_{\rm f} = 1.86 \; {\rm K} \; {\rm m}^{-1})$			carbamide, then the molecula
	(1) -1.86°C (2) -0.93°C (3) -0.093°C (4) 0.093°C		weight of thiocarbamide i	
			(1) 152 (2) 760	(3) 60 (4) 180
125.	The freezing point of 1 m NaCl solution assuming NaCl to	135.	The osmotic pressure of	of a sugar solution at 24°C i
	be 100% dissociated in water is $(K_f = 1.86 \text{ K m}^{-1})$			of the solution in mole per litter
	(1) -1.86°C $(2) -3.72$ °C $(3) +1.86$ °C $(4) +3.72$ °C		(1) 10.25 (2) 1.025	(3) 1025 (4) 0.1025
126.	The molal freezing point constant of water is 1.86 K m ⁻¹ .	136.	The Van't Hoff factor of ve	ery dilute solution of Ca(NO ₃).
	If 342 g of cane sugar $(C_{12}H_{22}O_{11})$ is dissolved in 1000 g		(1) 1 (2) 2	(3) 3 (4) 4
	of water, the solution will freeze at	137.	Lowering in vapour press	ure is highest for
	(1) -1.86°C $(2) 1.86$ ° $(3) -3.92$ °C $(4) 2.42$ °C		(1) 0.2 m urea	(2) 0.1 m glucose
127.	The osmotic pressure of a solution containing 0.1 mol of		(3) 0.1 m MgSO ₄	(4) 0.1 m BaCl ₂
	solute per litre at 273 K is	138.	Which of the following w	rill have the highest boiling pour
	0.1		at 1 atm pressure?	
	(1) $\frac{0.1}{1} \times 0.08205 \times 273$ atm		(1) 0.1 M NaCl	(2) 0.1 M sucrose
	(2) $0.1 \times 2 \times 0.08205 \times 273$ atm		(3) 0.1 M BaCl ₂	(4) 0.1 M glucose
		139.	An aqueous solution free:	zes at
	(3) $\frac{1}{0.1} \times 0.08205 \times 273$ atm		-0.186 °C ($K_c = 1.86$ °; K_L	$= 0.512^{\circ}$). What is the elevation
	0.1		in boiling point?	
	(4) $\frac{0.1}{1} \times \frac{273}{0.08205}$ atm		(1) 0.186 (2) 0.512	(3) $\frac{0.512}{1.86}$ (4) 0.0512
128	1 0.00203	1.10	(1) 0.100 (2) 0.512	1.86 1.86°C. Th
120.	The osmotic pressure of 40% (weight/volume) urea solution is 1.64 atm and that of 3.42% (weight/volume) cane sugar is	140.	Ine molal depression co	1.86 onstant for water is 1.86°C. The post of a non-electroly
	2.46 atm. When equal volumes of the above two solutions		neezing point of a 0.05-n	nolal solution of a non-electroly
	are mixed, the osmotic pressure of the resulting solution is		in water is	
			(1) -1.86°C $(2) -0.93$ °C	C (3) -0.093 °C (4) 0.93 °C
120	(1) 1.64 atm (2) 2.46 atm (3) 4.10 atm (4) 2.05 atm	141.	. The freezing point of a s	solution prepared from he mol
129.	The osmotic pressure of a solution (density is 1 g mL ⁻¹)		non-electrolyte and 20 g	of water is 271.9 K. If the mole 6 K mol ⁻¹ , then molar mass of the mole of t
	containing 3 g of glucose (molecular weight = 180) in		depression constant is 1.8	6 K mol ⁻¹ , then molar mass

solute will be

(2) 106.7

(4) 93.9

(1) 105.7

(3) 115.3

60 g of water at 15°C is

 $(1)\ 0.34\ atm\quad (2)\ 0.65\ atm\quad (3)\ 6.25\ atm\quad (4)\ 5.57\ atm$

142. A 5% solution of cane sugar (molecular weight = 342) is isotonic with 1% solution of substance X. The molecular weight of X is

(1) 171.2

(2)68.4

- (3) 34.2
- (4) 136.2
- The osmotic pressure of blood is 7.40 atm at 27°C. The number of mol of glucose to be used per litre for an intravenous injection that is to have the same osmotic pressure as blood is

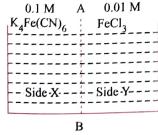
(1) 0.3

- (2) 0.2
- (3) 0.1
- (4) 0.4
- 144. PtCl₄.6H₂O can exist as a hydrated complex; 1 m aqueous solution has the depression in freezing point of 3.72 K. Assume 100% ionization and K_f (H₂O) = 1.86 Km⁻¹, then the complex is

(1) $[Pt(H_2O)_6]Cl_4$

- (2) [Pt(H₂O)₄Cl₂]Cl₂·2H₂O
- $(3) [Pt(H_2O)_3Cl_3]Cl \cdot 3H_2O$ (4) $[Pt(H_2O)_2Cl_4] \cdot 4H_2O$
- 145. Which of the following solutions (1 molal) will have the maximum freezing point, assuming equal ionization in each case?
 - (1) $[Fe(H_2O)_6]Cl_3$
- (2) [Fe(H₂O)₅Cl]Cl₂·H₂O
- (3) $[Fe(H_2O)_4Cl_2]Cl\cdot 2H_2O$ (4) $[Fe(H_2O)_3Cl_3]\cdot 3H_2O$
- 146. The depression in freezing point of 0.01 m aqueous CH, COOH solution is 0.02046°. 1 m urea solution freezes at -1.86°C. Assuming molality equal to molarity, pH of CH3COOH solution is
 - (1)2
- (2)3
- (3) 3.2
- (4) 4.2
- 147. pH of a 0.1 M monobasic acid is found to be 2. Hence, its osmotic pressure at a given temperature TK is
 - (1) 0.1RT (2) 0.11RT (3) 1.1RT

- $(4) \ 0.01RT$
- 148. The lowering of vapour pressure due to a solute in a 1 m aqueous solution at 100°C is
 - (1) 13.44 torr
- (2) 14.12 torr
- (3) 312 torr
- (4) 352 torr
- 149. Which has the maximum osmotic pressure at temperature T?
 - (1) 100 mL of 1 M urea solution.
 - (2) 300 mL of 1 M glucose solution.
 - (3) Mixture of 100 mL of 1 M urea solution and 300 mL of 1 M glucose solution.
 - (4) All are isotonic.
- 150. $FeCl_3$ on reaction with $K_4[Fe(CN)_6]$ in aqueous solution gives blue colour. These are separated by a semi-permeable membrane AB as shown. Due to osmosis, there is



- (1) Blue colour formation in side X.
- (2) Blue colour formation in side Y.
- (3) Blue colour formation in both of sides X and Y.
- (4) No blue colour formation.

- **151.** 12.2 g of benzoic acid (Mw = 122) in 100 g benzene has depression in freezing point 2.6°; $K_f = 5.2^{\circ} \text{ kg mol}^{-1}$. If there is 100% polymerzation, the number of molecules of benzoic acid in associated state is
 - (1) 1
- (2)2
- (3)3
- (4)4
- 152. 25 mL of an aqueous solution of KCl was found to require 20 mL of 1 M AgNO₃ solution when titrated using a K₂CrO₄ as indicator. The depression in freezing point of KCl solution with 100% ionization will be:

 $[K_f = 2.0^{\circ} \text{ mol}^{-1} \text{ kg and molarity} = \text{molality}]$

- $(1) 5.0^{\circ}$
- $(2) 3.2^{\circ}$
- $(3) 1.6^{\circ}$

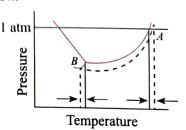
For Problems 153–155

Following questions are based on the following activities (A) with observations (O) and results or reason (R),

- (1) If A and O are correct and R is incorrect, mark (1).
- (2) If A and O are incorrect and R is correct, mark (2).
- (3) If A, O, and R are all correct, mark (3).
- (4) If A is correct, and O and R are incorrect, mark (4).

	Activity (A)	Observation (O)	Result/ reason (R)
153.	0.01 M K ₃ [Fe(CN) ₆] and 0.1 M FeCl ₃ solutions are separated by a semi-permeable membrane.	Osmosis takes place from 0.01 M solution to 0.1 M solution but no blue colour formation either of side.	Osmosis takes place from dilute to concentrated solution and the solvent (H ₂ O) that flows.
154.	1 mol each of benzene and toluene are mixed.	$P_{\text{total}}^{\circ} = P_{B}^{\circ} \chi_{B} + P_{T}^{\circ} \chi_{T}$	This is positive deviation from Raoult's law.
155.	Ether is added to H ₂ O.	Boiling point is elevated	Boiling point is elevated when a volatile solute is added to a solvent.

- 156. The amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to -9.3°C is: $(K'_f = 1.86 \text{ K molality}^{-1})$
 - (1) 38.71 g
- (2) 38.71 mg
- (3)42g
- (4) 42 mg
- 157. The phase diagrams for a pure solvent (represented by the solid line) and a corresponding solution (containing a nonvolatile solute and represented by the dashed lines) are shown below.

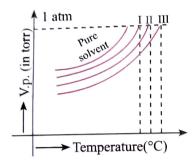


Choose the correct option.

- (1) $A = \Delta T_b m$ and $B = \Delta T_f m$
- (2) $A = \Delta T_f m$ and $B = \Delta T_b m$
- (3) $A = \Delta T_f$ and $B = \Delta T_b$
- (4) $A = \Delta T_b$ and $B = \Delta T_f$

where T_f T_b and m stand for freezing point temperature, boiling point temperature and molality.

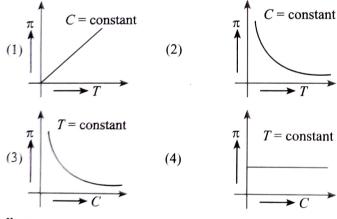
158. The vapour pressure curves of the same solute in the same solvent are shwon below. The curves are parallel to each and do not intersect. The concentrations of solutions are in order of:



- (1) I < II < III
- (2) I = II = III
- (3) I > II > III
- (4) I > III > II
- 159. van't Hoff proved that osmotic pressure (π) is a colligative property. For an ideal solution, osmotic pressure (π) is helpful to determine that molecular mass of solute using W_RT

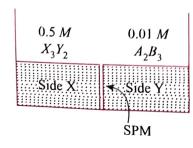
$$M_{\rm B} = \frac{W_B RT}{\pi \cdot V}$$

Relation cna be expressed by the curve (C = concentration):



Miscellaneous

160. X_3Y_2 (i = 5) when reacted with A_2B_3 (i = 5) in aqueous solution gives brown colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is:



- (1) Brown colour formation in side X
- (2) Brown colour formation in side Y
- (3) Formation in both of the sides X and Y
- (4) No brown colour formation
- 161. The osmotic pressure of 0.3 M aqueous solution of NaClis equal to the osmotic pressure of 0.2 M aqueous solution of unknown ionic compound X. The van't Hoff factor of χ_{is}
 - (1) 1.0

(2) 1.5

(3) 2.5

- (4) 3.0
- 162. At 760 torr pressure and 20°C temperature, 1 L of water dissolves 0.04 gm of pure oxygen or 0.02 gm of pure nitrogen. Assuming that dry air is composed of 20% oxygen and 80% nitrogen (by volume), the masses in g/L) of oxygen and nitrogen dissolved by 1 L of water at 20°C exposed to air at a total pressure of 760 torr are respectively:
 - (1) 0.008, 0.016
- (2) 0.016, 0.008
- (3) 0.16, 0.08
- (4) 0.04, 0.02
- 163. At 300 K, 40 mL of O₃(g) dissolves in 100 g of water at 1.0 atm. What mass of ozone dissolved in 400 g of water at a pressure of 4.0 atm at 300 K?
 - (1) 0.1 g

- (2) 1.24 g
- (3) 0.48 g
- (4) 4.8 g
- 164. According to henry's law, the partial pressure of gas (P) is directly proportional to mole fraction of gas in liquid solution, $P_{\rm gas} = K_H \cdot X_{\rm gas}$, where K_H is Henry's constant Select **incorrect** statement?
 - (1) K_H is characteristic constant for a given gas-solven system
 - (2) Higher is the value of K_H , lower is solubility of gas \hat{w} a given partial pressure of gas
 - (3) K_H has temperature dependence
 - (4) K_H decreases with increase of temperature
- 165. According to Henry's law, the solubility of a gas in given volume of liquid increases with increase in:
 - (1) Temperature
- (2) Pressure
- (3) Both (1) and (2)
- (4) None of these
- 166. 1 kg of water under a nitrogen pressure of 1 atmosphere dissolves 0.02 gm of nitrogen at 293 K. Calculate Henry's law constant:
 - (1) 7.7×10^4 atm
- (2) 7.7×10^3 atm
- (3) 2×10^{-5} atm
- (4) 2×10^{-2} atm
- 167. The freezing point of the solution of compound (N) Co(NH₃)₄Cl₃, containing 23.35 of solute per kg water is

Given: $K_f = 1.86^{\circ} c/m$.

Mw of $X = 233.5 \text{ g mol}^{-1}$

- (1) -0.186 °C
- (2) -0.372°C
- (3) -0.558°C
- (4) -0.744°C

Select the INCORRECT statement about solubility of gases and Henry's constant: gases and Henry's constant:

- (1) Partial pressure of a gas is related to number of moles of the dissolved gas and $K_{\rm H}$ (Henry's constant)
- (2) O₂(g) and N₂(g) are less soluble in H₂O and solubility of these gases decrease with increase of temperature. These gases have higher $K_{\rm H}$ value at a given pressure and $K_{\rm H}$ value increase with temperature
- (3) SO₂(g) and NH₃(g) are more soluble in H₂O and solubility of these gases decrease with increase of temperature. These gases have lower $K_{\rm H}$ value at a given pressure.
- (4) Helium (g) and Argon (g) are sparingly soluble in acetone and solubility of these gases increases slightly with increase of temperature. These gases have higher $K_{\rm H}$ value at a given pressure.
- 169. The van't Hoff factor (i) for the following are respectively, if 60% ionisation or association takes place.
 - I. Hg,Cl, in aqueous solution.
 - II. Boron in non-aqueous solution
 - (1) 2.2, 0.45
- (2)054
- (3) 2.8, 0.55
- (4) 3, 0.5
- 170. If the boiling point of an aqueous solution is 100.3°C. Given l_f and l_g are 100 and 500 cal g^{-1} respectively. (l_f and l, are latent heat of fusion and vapourization respectively) Select the CORRECT experssion for ΔT_f

$$(1) \Delta T_{\rm f} = \frac{(273)^2 \times 1.5}{(373)^2}$$

(1)
$$\Delta T_f = \frac{(273)^2 \times 1.5}{(373)^2}$$
 (2) $\Delta T_f = \frac{(273)^2 \times 0.5}{(373)^2}$

(3)
$$\Delta T_f = \frac{(373)^2 \times 1.5}{(273)^2}$$

(3)
$$\Delta T_f = \frac{(373)^2 \times 1.5}{(273)^2}$$
 (4) $\Delta T_f = \frac{(373)^2 \times 0.5}{(273)^2}$

Multiple Correct Answers Type

Raoult's Law, Ideal and NonIdeal Solution, Azeotrope

- 1. Two miscible liquids A and B having vapour pressure in pure state P_A° and P_B° are mixed in mole fraction χ_A and λ_B to get a mixture having total vapour pressure of mixture $P_{\rm M}$. Which of the following relations are correct?
 - (1) $\chi_{A} = \frac{P_{M} P_{B}^{\circ}}{P_{A}^{\circ} P_{B}^{\circ}}$ (2) $\frac{\chi_{A(l)}}{\chi'_{A(V)}} = \frac{P_{M}}{P_{A}^{\circ}}$
- - $(3) \frac{\chi_{A(l)}}{\chi'_{A(V)}} = \frac{P_{M}}{P_{B}}^{\circ}$
- (4) All of these
- 2. A mixture of two immiscible liquids A and B, having vapour pressure in pure state obeys the following relationship if χ_A and χ_B are mole fractions of A and B in vapour phase over the solution
 - $(1) P'_{A} = P_{M} \chi'_{A}$

$$(2) \frac{P_{\rm A}'}{P_{\rm B}'} = \frac{W_{\rm A} \times M w_{\rm B}}{M w_{\rm A} \times W_{\rm B}}$$

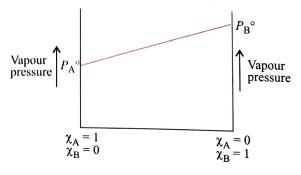
- (3) If $P'_A > P'_B$ then $\chi'_A < \chi'_B$
- (4) If $P'_A > P'_B$, then $n_A > n_B$
- 3. Which relations are not correct for an aqueous dilute solution of K_3PO_4 if its degree of dissociation is α ?

(1)
$$\frac{\Delta P}{P^{\circ}} = \frac{\text{Molality} \times 18 \times (1 + 3\alpha)}{1000}$$

(2)
$$\frac{\Delta P}{P^{\circ}} = \frac{\pi_{\text{obs}} \times 18 \times (1 + 3\alpha)}{RT \times 1000}$$

$$(3) \frac{\Delta P}{P^{\circ}} = \frac{\Delta T_{\text{f obs}} \times 18}{K_{\text{f}} \times 1000}$$

- (4) $Mw \text{ of } K_3PO_4 = Mw_{obs} \times (1 + 3\alpha)$
- **4.** Which of the following statements is/are correct?
 - (1) Minimum boiling azeotropic mixture boils at temperature lower than either of the two pure components.
 - (2) Maximum boiling azeotropic mixture boils at temperature higher than either of the two pure components.
 - (3) Minimum boiling azeotropic mixture shows positive deviation.
 - (4) Maximum boiling azeotropic mixture shows negative deviation.
- 5. For a non-volatile solute
 - (1) The vapour pressure of a solute is zero.
 - (2) Vapour pressure of solution = Vapour pressure of pure solvent.
 - (3) Vapour pressure of solution = Vapour pressure of solvent in solution.
 - (4) All of these.
- **6.** 1 mol benzene $(P^{\circ}_{\text{benzene}} = 42 \text{ mm})$ and 2 mol toluene $(P_{\text{toluene}}^{\circ} = 36 \text{ mm}) \text{ will have}$
 - (1) Total vapour pressure of 38 mm.
 - (2) Mole fraction of vapour of benzene above liquid mixture is 7/19.
 - (3) Positive deviation from Raoult's law.
 - (4) Negative deviation from Raoult's law.
- 7. Which pair(s) of liquids on mixing is/are expected to show no net volume change and no heat effect?
 - (1) Acetone and ethanol
 - (2) Chlorobenzene and bromobenzene
 - (3) Chloroform and benzene
 - (4) *n*-Butyl chloride and *n*-butyl bromide
- 8. The following is a graph plotted between the vapour pressure of two volatile liquids against their respective mole fractions.

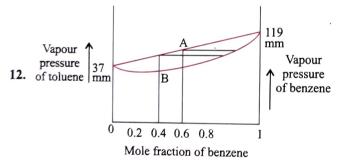


Which of the following statements is/are correct?

- (1) When $\chi_A = 1$ and $\chi_B = 0$, then $P = P_A^{\circ}$.
- (2) When $\chi_B = 1$ and $\chi_A = 0$, then $P = P_B^{\circ}$.
- (3) When $\chi_A = 1$ and $\chi_B = 0$, then $P < P_B^{\circ}$.
- (4) When $\chi_B = 1$ and $\chi_A = 0$, then $P > P_A^{\circ}$.
- 9. Which of the following combinations are correct for a binary solution, in which the solute as well as solvent are liquid?
 - (1) C_6H_6 and $C_6H_5CH_3$; $\Delta_{sol}H > 0$; $\Delta_{sol}V = 0$

(2) CH₃ — C —CH₃ and CHCl₃;
$$\Delta_{\rm sol}H < 0$$
; $\Delta_{\rm sol}V < 0$

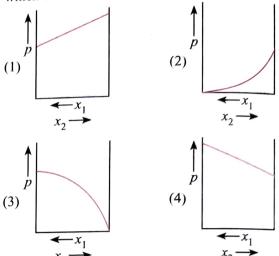
- (3) H_2O and HCl; $\Delta_{\text{sol}}H > 0$; $\Delta_{\text{sol}}V < 0$
- (4) H₂O and CH₃OH; $\Delta_{sol}H > 0$; $\Delta_{sol}V < 0$
- 10. Effect of adding a non-volatile solute to a solvent is:
 - (1) to lower the vapour pressure
 - (2) to increase its freezing point
 - (3) to increase its boiling point
 - (4) to decrease its osmotic pressure
- 11. Which of the following forms is an ideal solution?
 - (1) Ethyl bromide + Ethyl iodide
 - (2) Ethyl alcohol + Water
 - (3) Chloroform + Benzene
 - (4) Benzene + Toluene



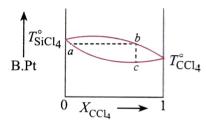
Choose the correct option:

- (1) A represents vapour composition and B represents liquid composition.
- (2) A as well as B represent liquid composition.
- (3) both A and B represent vapour composition.
- (4) A represents liquid composition and B represents vapour composition.
- When acetone and chloroform are mixed, hydrogen bonding takes place between them. Such a liquid pair will cause
 - (1) Positive deviation from Raoult's law.
 - (2) Negative deviation from Raoult's law.
 - (3) No deviation from Raoult's law.
 - (4) Cannot be predicted.
- 14. A maxima or minima is obtained in the temperature. The composition curve of a mixture of two liquids does not indicate
 - (1) That the liquids are immiscible with one another
 - (2) That the liquids are partially miscible at the maximum or minimum.

- (3) An azeotropic mixture.
- (4) A eutectic formation.
- 15. For a binary ideal liquid solution, the variation in total vapour pressure versus composition of solution is given by which of the curves?



16. The diagram given below depicts the boiling point as the function of composition of the mixture of CCl₄ and SiCl₄. Which of the following statements about the diagram is/are true?



- (1) The point a represents the composition of solution and the point b that of the vapour in equilibrium
- (2) The proportion of CCl₄ in the solution is smaller than that in the vapour in equilibrium
- (3) bc represents the condensation of the vapour
- (4) The point c represents the composition of soution and the point b that of the vapour in equilibriums.
- 17. On mixing 1 mole of C_6H_6 ($P^0 = 42$ mm) and 2 mole of C_7H_8 ($P^0 = 36$ mm), one can conclude:
 - (1) Total vapour pressure of mixture = 38 mm
 - (2) Mole fractoin of vapours of C_6H_6 above liquid mixture $= \frac{7}{10}$
 - (3) Positive deviation from Raoult's law
 - (4) Both forms ideal solution
- 18. Composition of an azeotrope
 - (1) Is independent of external pressure because it is is compound
 - (2) Alters on changing the external pressure as it is not a compound
 - (3) Remains unchanged during distillation at a constant external pressure
 - (4) Fluctuates even at constant pressure

- 19. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are):
 - (1) ΔG is positive
- (2) ΔS_{system} is positive
- (3) $\Delta S_{\text{surroundings}} = 0$
- $(4) \Delta H = 0$
- Which of the following statements is/are wrong for a solution of chloroform and acetone?
 - (1) The solution formed is an ideal solution
 - (2) The solution formed is a non-ideal solution with positive deviation from Raoult's law
 - (3) The solution formed is a non-ideal solution with negative deviation from Raoult's law
 - (4) The solution behaves ideally or non-ideally depending upon its composition

Colligative Properties and Vant Hoff factor

- 21. Osmotic pressure of a solution is
 - (1) Directly proportional to the molar concentration of the solution.
 - (2) Inversely proportional to the molecular weight of the solute.
 - (3) Inversely proportional to the temperature.
 - (4) Directly proportional to the volume of the solution.
- 22. Which of the following is/are true?
 - (1) For the same solution, elevation in boiling point = depression in freezing point.
 - (2) The Van't Hoff factor for a dilute solution of BaCl₂ is 3.
 - (3) The elevation in boiling point is due to increase in vapour pressure.
 - (4) The depression in freezing point is due to decrease in vapour pressure.
- 23. To 10 mL of 1 M BaCl₂ solution 5 mL of 0.5 M K₂SO₄ is added. BaSO₄ is precipitated out. What will happen?
 - (1) Freezing point will increase.
 - (2) Boiling point will increase.
 - (3) Freezing point will lower down.
 - (4) Boiling point will lower down.
- 24. A difference between diffusion and osmosis is
 - (1) A semi-permeable membrane is required for osmosis while diffusion requires no semi-permeable membrane.
 - (2) In osmosis movement of molecules is only in one direction whereas in diffusion movement is on both sides.
 - (3) In osmosis only the solvent moves while in diffusion both solute and solvent move.
 - (4) None of these.
- 25. Which of the following statements is/are correct?
 - (1) The freezing point of water is depressed by the addition of glucose.
 - (2) The degree of dissociation of a weak electrolyte decrease as its concentration decreases.
 - (3) Energy is released when a substance dissolves in water provided that the hydration energy of the substance is more than its lattice energy.

- (4) If two liquids that form an ideal solution are mixed, the change in entropy is positive.
- **26.** Consider the two solutions:
 - I: 0.5 M NaCl aqueous solution at 25°C;

NaCl is completely ionized.

II:2.0 M C₆H₅COOH in benzene at 25°C,

C₆H₅COOH dimerizes to the full extent.

- Which of the following statements(s) is(are) correct? (1) Both the solutions display equal osmotic pressure.
- (2) Both have equal vapour pressure.
- (3) Solution II is hypertonic.
- (4) Solution II has greater depression in freezing point than solution I.
- 27. Consider the following solutions:
 - I. 1 M sucrose

II. 1 M KCl

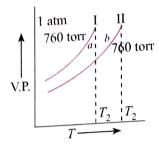
III. 1 M benzoic acid in benzene

IV. 1 M $(NH_4)_3PO_4$

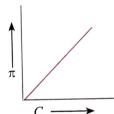
Which of the following is/are true?

- (1) All solutions are isotonic.
- (2) III is hypotonic of I, II, and IV.
- (3) I, II, and III are hypertonic of IV.
- (4) IV is hypertonic of I, II, and III.
- 28. The osmotic pressure of a solution depends on
 - (1) Nature of solute
 - (2) Nature of solvent
 - (3) Temperature
 - (4) Molar concentration of solute
- 29. 1.2575 g sample of $[Cr(NH_3)_6]SO_4Cl$ (Mw = 251.5) is dissolved to prepare 250 mL solution showing an osmotic pressure of 1.478 atm of Hg at 27°C. Which of the following statements is/are correct about this solution?
 - (1) Each molecule furnishes three ions in solution.
 - (2) The Van't Hoff factor is = 3.
 - (3) The equilibrium molarity of $[Cr(NH_3)_6]SO_4Cl = 0$.
 - (4) The equilibrium molarity of $[Cr(NH_3)_6]^{3+} = 0.02 \text{ M}.$
- 30. 2 L of 1 molar solution of a complex salt CrCl₃.6H₂O (Mw = 266.5) shows an osmotic pressure of 98.52 atm. The solution is now treated with 1 L of 6 M AgNO₃, which of the following are correct?
 - (1) Weight of AgCl precipitated is 861 g.
 - (2) The clear solution will show an osmotic pressure of 98.52 atm.
 - (3) The clear solution will show an osmotic pressure of 65.68 atm.
 - (4) 2 mol of [Cr(H₂O)₆] (NO₃)₃ will be present in the solution.
- 31. For a given value of degree of dissociation, which of the following have correct Van't Hoff factor?
 - (1) NaCl, $i = 2 + \alpha$

- (2) $Ca(NO_3)_2$, $i = 1 + 2\alpha$
- (3) $K_4[Fe(CN)_6]$, $i = 1 + 4\alpha$
- (4) $(NH_4)_3 PO_4$, $i = 3 + \alpha$
- 32. Vapour pressure-temperature curves of pure solvent and a solution containing a non-volatile solute are shown in the figure. Select the correct statement(s)



- (1) Curve I represents the variation of vapour pressure of solution and II that of solvent with temperature
- (2) Curve I and II represents the variation of vapour pressures of solvent and solution respectively with temperature
- (3) Gap ab represents K_b m for the solution
- (4) Gab ab represents $K_{\rm f}$ m for the solution
- 33. A graph showing variation of osmotic pressure (π) versus molar concentration (C) of an aqueous solution at temperature T is given below:



The slope of the line doesn't represent:

- (1) Solution constant R
- (2) Absolute temperature T
- (3) RT
- (4) Degree of ionization of solute?

Linked Comprehension Type

Paragraph 1

The osmotic pressure π depends on the molar concentration of the solution ($\pi = CRT$). If two solutions are of equal solute concentration and, hence, have the same osmotic pressure, they are said to be isotonic. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be hypertonic and the more diluted solution is described as hypotonic.

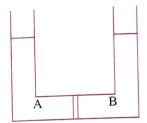
Osmosis is the major mechanism for transporting water upward in the plants. Answer the following questions:

- 1. A plant cell shrinks when it is kept in:
 - (1) Hypotonic solution
- (2) Hypertonic solution
- (3) Isotonic solution
- (4) Pure water

- 2. What would be the percent strength of solution of ureally with 4.5% solution of glucoses would be isotonic with 4.5% solution of glucose? (2) 13.5%
 - (1) 4.5%

- (3) 1.5%
- (4) 9%
- 3. The glucose solution to be injected into the bloodstream the blood itself should have the same
 - (1) Molarity
- (2) Vapour pressure
- (3) Osmotic pressure
- (4) Viscosity
- 4. Isotonic solutions have same
 - (1) Density
- (2) Molarity
- (3) Molality
- (4) Normality
- (5) Osmotic pressure
- 5. Osmotic rise of a solution depends on
 - (1) Concentration
- (2) Temperature
- (3) Nature of solvent
- (4) All of these

Paragraph 2



Compartments A and B have the following combinations solution:

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\Box		

- 1. 0.1 M KCl
- B 0.2 M KCl
- 2. 0.1% (m/V) NaCl
- 10% (m/V) NaCl
- 3. 18 g L⁻¹ glucose
- 34.2 g L⁻¹ sucrose
- 4. 20% (m/V) glucose
- 10% (m/V) glucose

Answer the following questions:

- 6. Indicate the number of solutions which is/are isotonic.
 - (1) 1 only
- (2) 3 only
- (3) 4 only
- (4) 2 only
- 7. The solutions in which compartment B is hypertonic.
 - (1) 1, 2

(2) 2, 3

(3)3,4

- (4) 1, 4
- 8. Indicate the solution(s) in which compartment A will show an increase in volume.
 - (1)4

(2)2

(3)3

- (4)5
- 9. Indicate the solution(s) in which compartment B will show an increase in volume.
 - (1) 1, 2, 4
- (2)1,2

(3)2,3

- (4) 3, 4
- 10. The solution in which there will be no change in the left of the solution. of the solution in the compartments A and B is.
 - (1) 1

(2) 2

(3)4

(4) 3

Paragraph 3

A solution M is prepared by mixing ethanol and water. The fine fraction of ethanol is at fraction of ethanol in the mixture is 0.9

Given: Freezing point depression constant of water $(K_{\rm f}^{\rm water}) = 1.86 \text{ K kg mol}^{-1}$ Freezing point depression constant of ethanol $(K_f^{\text{ethanol}}) = 2.0 \text{ K kg mol}^{-1}$ Boiling point elevation constant of water

 $(K_b^{\text{water}}) = 0.52 \text{ K kg mol}^{-1}$

Boiling point elevation constant of ethanol $(K_b^{\text{ethanol}}) = 1.2 \text{ K kg mol}^{-1}$

Standard freezing point of water = 273 K Standard freezing point of ethanol = 155.7 K Standard boiling point of water = 373 K Standard boiling point of ethanol = 351.5 K Vapour pressure of pure water = 32.8 mm Hg Vapour pressure of pure ethanol = 40 mm Hg Molecular weight of water = 18 g mol⁻¹

Molecular weight of ethanol = 46 g mol⁻¹ In answering the following questions consider the solutions to he ideal dilute solutions and solutes to be non-volatile and nondissociative.

- 11. The freezing point of the solution M is
 - (1) 268.7 K
- (2) 268.5 K
- (3) 150.9 K
- (4) 268.7 K
- 12. The vapour pressure of the solution M is
 - (1) 39.3 mm Hg
- (2) 36.0 mm Hg
- (3) 29.5 mm Hg
- (4) 28.8 mm Hg
- 13. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is
 - (1) 380.4 K
- (2) 376.2 K
- (3) 375.5 K
- (4) 354.7 K

Paragraph 4

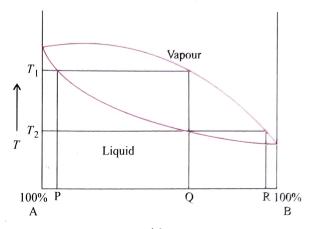
A certain vessel X has water and nitrogen gas at a total pressure of 2 atm and 300 K. All the contents of vessel are transferred to another vessel Y having half the capacity of the vessel X. The pressure of N_2 in this vessel was 3.8 atm at 300 K. The vessel Y is heated to 320 K and the total pressure observed was 4.32 atm. Assume that the volume occupied by the gasses in vessel is equal to the volume of the vessel. Calculate the following:

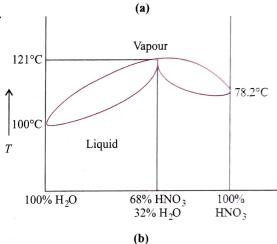
- 14. Pressure of $H_2O(g)$ in X at 320 K.
 - (1) 0.1

- (2) 0.2
- (3) 1.0
- (4) 2.0
- 15. Pressure of N_2 at 320 K.
 - (1)4.0
- (2)4.05
- (3) 5.05
- (4) 1.05
- $16. P_{ressure}$ of water vapour at 320 K
 - (1) 0.27
- (2) 0.32
- (3)4.0
- (4) 1.0
- 17. Enthalpy of vapourization.
 - (1) 30.00
- (2) 35.65
- (3) 38.65
- (4)39.65

Paragraph 5

Figure (a) represents the distillation of mixture of liquid A and liquid B which gives both of pure liquid A and B. While Fig. (b) represents the azeotopic mixture of HNO3 and H2O which distillation gives an azeotropic mixture and either of pure liquid. We cannot separate both the pure liquid, i.e., H₂O and HNO₃.





- 18. What is the result of distilling a mixture of 50% HNO, and 50% H₂O?
 - (1) Pure water and azeotropic mixture can be separated.
 - (2) Pure H₂O and pure HNO₃ can be separated.
 - (3) Pure HNO₃ and azeotropic mixture can be separated.
 - (4) None of these
- 19. What is the result of distilling a mixture of 80% HNO, and 20% H₂O?
 - (1) Pure H₂O and azeotropic mixture can be separated.
 - (2) Pure H₂O and pure HNO₃ can be separated.
 - (3) Pure HNO₃ and azeotropic mixture can be separated.
 - (4) None of these
- 20. Which of the following statements is/are correct?
 - i. HNO₃ solution is not obeying the Raoult's law.
 - ii. More the difference in vapour pressure of pure compounds forming a mixture, easier to separate them through distillation.
 - iii. In Fig. (a), T_2 is less than T_1 because the liquid of composition Q is richer in more volatile component.
 - (1) (ii) and (iii)
- (2) (ii)
- (3) (i) and (ii)
- (4) (i), (ii) and (iii)

- 21. In Fig. (a), a solution of 50% of A and 50% of B on distillation results into
 - (1) Separation of an azeotropic mixture and pure A.
 - (2) Separation of an azeotropic mixture and pure B.
 - (3) Separation of both pure A and pure B.
 - (4) None of these
- 22. At temperature T_1 and composition Q, which of the following is true?
 - (1) Vapour phase is richer in B while liquid phase is richer in A.
 - (2) Distillation of composition Q gives only pure A.
 - (3) Distillation of composition Q gives pure A and pure B.
 - (4) Distillation of composition Q gives higher percentage of B than A.

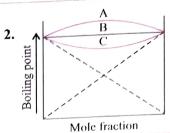
Matrix Match Type



This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

1. p_A = partial pressure of component A in liquid mixture, P_A° = vapour pressure of A, χ_A = mole fraction of A in liquid mixture

	Column I		Column II
a.	$C_2H_5OH + H_2O$	p.	Azeotropic mixture
	$C_2H_5Br + C_2H_5I$	q.	Obeys Raoult's law
	$p_A = \chi_A P_A^{\circ}$	r.	Non-ideal solution with positive deviation
d.	$H_2O + H_2SO_4$	s.	Non-ideal solution with negative deviation
	e de la compania del compania del compania de la compania del compania de la compania del compania de la compania del compania del compania del compania del la compania del compania dela compania del compania del compania del compania del compania de	t.	Ideal solution



Column I			Column II
a.	A	p.	(+) deviation
b.	В	q.	Ideal
c.	C	r.	(-) deviation

3. Match the following:

	Column I		Column I
a.	Urea, glucose, fructose		1:0.8:1
b.	NaCl, MgCl ₂ , K ₂ SO ₄	q.	1:2:3
	$Al_2(SO_4)_3$, Na_3PO_4 , $K_4[Fe(CN)_6]$	r.	1:1:1
	Glucose, NaCl, CaCl ₂	S.	2:3:3

4

	Column I	7	Column II
a.	Hypertonic	p.	Solutions having same osmotion pressure
b.	Isotonic	q.	One solution has higher osmotic pressure than the second solution.
c.	Van't Hoff	r.	Theory of dilute solution
d.	Beckmann	s.	Differential thermometer

5.

5.		Column I		Column II
2.0	a.	$P^{\circ} - P_{\rm s}$	p.	Observed colligative property Normal colligative property
	b.	$P^{\circ} \times \chi_{A} = P_{A}$	q.	Lowering in vapour pressure
-	c.	Mixture that boils like pure solvent	r.	Azeotropic mixture
	d.	Van't Hoff factor	s.	Raoult's law

6.

	Compounds		Characteristics (I)		Characteristics (II)
a	Brass	i	Interstitial solid solution	p	Formed by placing atoms of one kind into the pother substance in its crystal lattice
b	Tungsten carbide	ii	Substitutional solid solution	q	Formed by placing atoms of one kind into the the lattice of atoms of other substance
c	Na ₂ CO ₃ ·H ₂ O	iii	Solubility does not increase or decrease continuously	r	Hydration energy is less than lattice energy
d	NaNO ₃	iv	Solubility decreases continuously with increase of temperature	S	On heating change at a particular pemperatulone polymorphic form to another
e	CaCl ₂ ·6H ₂ O	v	Solubility increases continuously with increase of temperature	t	Process of dissolution is endothermic

	Gases		Characteristics (I)		Characteristics (II)
a	O ₂ and N ₂	i	More soluble in H ₂ O	p	Lower K _H (Henry's constant) value at a given pressure
b	SO ₂ and NH ₃	ii	Less soluble in H ₂ O	q	Higher K _H value at a given pressure
c	Helium and Ar	iii	Sparingly soluble in acetone. Solubility increases slightly with increase of temperature	r	K _H value increases with increase of temperature
d	Partial pressure of a gas is related	iv	Solubility of gases decreases with increase of temperature	s	Chemically react with water
		v	Mole fraction of the dissolved gas	t	K _H

Numerical Value Type

- 1. 12.2 g of benzoic acid (Mw = 122) in 100 g water has elevation in boiling point of 0.27. $K_b = 0.54 \text{ K kg mol}^{-1}$. If there is 100% polymerization, the number of molecules of benzoic acid in associated state is
 - (1) 2
- (2) 1
- (3) 3
- (4) 4
- 2. The ratio of the value of any colligative property for BaCl, solution of urea solution under similar condition is
 - (1)2
- (2) 3
- (3) 1
- (4)4
- 3. The Van't Hoff factor for a solute which does not dissociate or associate in solution is
 - (1)0
- (2)2
- (3)3
- (4) 1
- 4. Compound PdCl₄.6H₂O is a hydrated complex; 1 m aqueous solution of it has freezing point 269.28 K. Assuming

100% ionization of complex, calculate the number of ions furnished by complex in the solution.

- (1) 1
- (2) 2
- (3)4
- (4)0
- 5. The total number of colligative properties are
 - (1) 1
- (2) 2
- (3)3
- 6. If for a sucrose, elevation in boiling point is 1.0°C, then what will be the boiling point of NaCl solution for same molal concentration?
 - $(1) 1.0^{\circ}C$
- $(2) 2.0^{\circ}C$
- $(3) 3.0^{\circ} C$
- (4) 4.0°C
- 7. The osmotic pressure of urea solution at 10°C is 200 mm. becomes 105.3 mm when it is diluted and temperature raised to 25°C. The extent of dilution is
 - (1) 8 times (2) 5 times
- (3) 4 times
- (4) 2 times
- 8. The osmotic pressure of a solution containing 40 g of solute (molecular mass 246) per litre at 27°C is (R = 0.0822 atm) $L \text{ mol}^{-1}$

 - (1) 3.0 atm (2) 4.0 atm (3) 2.0 atm
- (4) 1.0 atm

Archives



JEE MAIN

Single Correct Answer Type

- 1. Two liquids X and Y form an ideal solution at 300 K, vapor pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapor pressure of the solution increases by 100 mm Hg. Vapor pressure (in mm Hg) of X and Y in their pure states will be, respectively
 - (1) 200 and 300
- (2) 300 and 400
- (3) 400 and 600
- (4) 500 and 600

(AIEEE 2009)

- 2. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behavior of the solution?
 - (1) The solution formed is an ideal solution
 - (2) The solution is non-ideal, showing positive deviation from Raoult's law
 - (3) The solution is non-ideal showing negative deviation from Raoult's law

(4) *n*-heptane shows positive deviation while ethanol shows negative deviation from Raoult's law

(AIEEE 2009)

- 3. A solution containing 2.675 g of CoCl₃.6NH₃ (molar mass = 267.5 g/mol) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g/mol). The formula of the complex is (atomic mass of Ag = 108 u)
 - (1) $[Co(NH_3)_6]Cl_3$
- (2) [CoCl₂(NH₃)₄]Cl
- (3) $[CoCl_3(NH_3)_3]$
- (4) [CoCl(NH₃)₅]Cl₃

(AIEEE 2010)

- 4. If sodium, sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water is $(K_f = 1.86 \text{ K.kg/mol})$
 - (1) 0.0372 K
- (2) 0.0558 K
- (3) 0.0744 K
- (4) 0.0186 K

(AIEEE 2010)

- 5. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at -6° C will be $(K_f \text{ for }$ water = 1.86 K.kg/mol and molar mass of ethylene glycol = 62 g/mol
 - (1) 804.32 g
- (2) 204.30 g
- (3) 400.00 g

- (AIEEE 2011) (4) 304.60 g
- **6.** The degree of dissociation (α) of a weak electrolyte $A_{\chi}B_{\gamma}$ is related to van't Hoff factor (i) by the expression

(1)
$$\alpha = \frac{i-1}{(x+y-1)}$$
 (2) $\alpha = \frac{i-1}{x+y+1}$
(3) $\alpha = \frac{x+y-1}{i-1}$ (4) $\alpha = \frac{x+y+1}{i-1}$

$$(2) \quad \alpha = \frac{i-1}{x+y+1}$$

$$(3) \quad \alpha = \frac{x + y - 1}{i - 1}$$

$$(4) \quad \alpha = \frac{x+y+1}{i-1}$$

(AIEEE 2011)

- 7. A 5% solution of cane sugar (molar mass = 342) is isotonic with 1% of a solution of a known solute. The molar mass of unknown solute in g/mol is
 - (1) 136.2
- (2) 171.2
- (3) 68.4
- (4) 34.2

(AIEEE 2011)

- 8. The molality of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm³ of water at STP is
 - (1) 0.555 m
- (2) 5.55×10^{-4} m
- (3) 33.3 m
- (4) 3.33×10^{-2} m

(AIEEE 2011)

- 9. Consider the separate solution of 0.500 M $C_2H_5OH(aq.)$, $0.100 \text{ M Mg}_3(PO_4)_2(aq.), 0.250 \text{ M KBr}(aq.) \text{ and } 0.125 \text{ M}$ Na₂PO₄(aq.) at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?
 - (1) They all have same osmotic pressure
 - (2) $0.100 \text{ M Mg}_3(PO_4)_2(aq.)$ has the highest osmotic pressure
 - (3) 0.125 M Na₃PO₄(aq.) has the highest osmotic pressure
 - (4) 0.5000 M C₂H₅OH(aq.) has the highest osmotic pres-(JEE Main 2014)
- 10. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substances was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol⁻¹) of the substance is:
 - (1) 32
- (2) 64
- (3) 128
- (4) 488
- (**JEE Main 2015**)
- 11. 18 g glucose $(C_6H_{12}O_6)$ is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution
 - (1) 759.0
- (2) 7.6
- (3) 76.0
- (4) 752.4

(JEE Main 2016)

- 12. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be:
 - $(K_{\epsilon} \text{ for benzene} = 5.12 \text{ K kg mol}^{-1})$
 - (1) 64.6%
- (2) 80.4%

(3) 74.6%

(JEE $_{Main 2017}$

- 13. For 1 molal aqueous solution of the following compounds which one will show the highest freezing point?
 - (1) $[Co(H_2O)_5Cl]Cl_2.H_2O$
 - (2) $[Co(H_2O)_4Cl_2]C\tilde{1}.2\tilde{H}_2O$
 - (3) $[Co(H_2O)_3Cl_3].3H_2O$
 - (4) $[Co(H_2O)_6]CI_3$

(JEE Main 2018

JEE ADVANCED

Single Correct Answer Type

- 1. Henry's law constant for the solubility of nitrogen gas in water at 298 K is 1.0×10^{-5} atm. The rnole fraction of nitrogen in air is 0.8. The number of moles of nitrogen from air dissolved in 10 mol of water at 298 K and 5 atm pressure
 - (1) 4.0×10^{-4} atm
- (2) 4.0×10^{-5} atm
- (3) 5.0×10^{-4} atm
- $(4) 4.0 \times 10^{-6}$ atm

(IIT-JEE 2009)

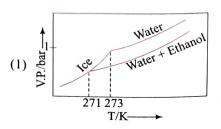
- 2. The freezing point (°C) of a solution containing 0.1 g of K₃[Fe(CN)₆] (molecular weight 329) in 100 g of water $(K_f = 1.86 \text{ K kg mol}^{-1}).$ (IIT-JEE 2011) (2) 5.7×10^{-2}
 - $(1) 2.3 \times 10^{-2}$
- (3) 5.7×10^{-3}
- $(4) -1.20 \times 10^{-2}$
- 3. For a dilute solution containing 2.5 g of a non-volatile nonelectrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take K,= $0.76 \text{ K kg mol}^{-1}$
 - (1)724
- (2)740
- (3)736
- (4)718

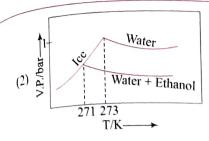
(IIT-JEE 2012)

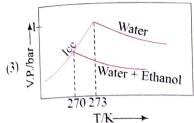
- 4. The vapour pressure of acetone at 20°C is 185 torr. What 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol⁻¹) of the substance is:
 - (1)32
- (2)64
- (3)128
- (4)488

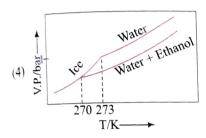
(JEE Advanced 2015)

5. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol⁻¹. The figure shown below represents plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ethanol is 46 g mol⁻¹] Among the following, the option representing change in the freezing point is -









(JEE Advanced 2017)

Multiple Correct Answers Type

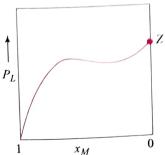
- 1. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are)
 - (1) ΔG is positive
 - (2) ΔS_{system} is positive
 - (3) $\Delta S_{\text{surrounding}} = 0$
 - $(4) \Delta H = 0$

(JEE Advanced 2013)

- 2. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are)
 - (1) carbon tetrachloride + methanol
 - (2) carbon disulphide + acetone
 - (3) benzene + toluene
 - (4) phenol + aniline

(JEE Advanced 2016)

3. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M, respectively, in the solution. The correct statement(s) applicable to this system is (are)



- (1) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed from $x_1 = 0$ to $x_2 = 1$
- (2) Attractive intermolecular interactions between L-L in pure liquid L and M-M in pure liquid M are stronger than those between L-M when mixed in solution
- (3) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_t \to 0$
- (4) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \to 1$

(JEE Advanced 2017)

Numerical Value Type

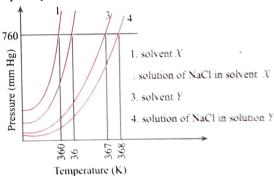
MX₂ dissociates into M²⁺ and X[⊙] ion in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in absence of ionic dissociation is

(JEE Advanced, 2014)

2. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. value of x_A/x_B in the new solution is _____. (given that the vapour pressure of pure liquid A is 20 Torr at temperature T)

(JEE Advanced 2018)

3. The plot given below shows *P*—*T* curves (where *P* is the pressure and *T* is the temperature) for two solvents *X* and *Y* and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is

(JEE Advanced 2018)

Answers Key

EXERCISES

Single Correct Answer Type

Single Con	rect Allswei	Type		
1.(2)	2. (2)	3. (2)	4. (2)	5. (2)
6.(1)	7. (2)	8. (1)	9. (1)	10. (1)
11.(2)	12.(3)	13. (1)	14. (1)	15. (1)
16.(2)	17. (2)	18. (1)	19. (2)	20. (2)
21.(1)	22.(1)	23. (4)	24. (3)	25. (1)
26. (4)	27. (3)	28. (3)	29. (1)	30. (2)
31. (2)	32.(1)	33. (2)	34. (4)	35. (2)
36. (2)	37. (4)	38. (2)	39. (1)	40. (1)
41.(1)	42.(1)	43. (3)	44. (4)	45. (1)
46.(1)	47. (3)	48. (2)	49. (2)	50. (3)
51.(2)	52. (1)	53. (4)	54. (4)	55. (3)
56. (4)	57. (2)	58. (4)	59. (2)	60. (3)
61. (4)	62. (4)	63. (3)	64. (3)	65. (2)
66. (3)	67. (4)	68. (4)	69. (3)	70. (3)
71.(2)	72. (3)	73. (3)	74. (2)	75. (1)
76. (2)	77. (2)	78. (4)	79. (1)	80. (1)
81. (3)	82. (4)	83. (4)	84. (1)	85. (1)
86. (1)	87. (1)	88. (3)	89. (4)	90. (4)
91. (3)	92. (2)	93. (4)	94. (2)	95. (1)
96. (1)	97. (1)	98. (2)	99. (2)	100. (1)
101. (1)	102. (2)	103. (3)	104. (3)	105. (4)
106. (1)	107. (2)	108. (4)	109. (3)	110. (3)
111. (3)	112. (1)	113. (1)	114. (1)	115. (2)
116. (1)	117. (4)	118. (1)	119. (3)	120. (3)
121. (1)	122. (4)	123. (3)	124. (3)	125. (2)
126. (1)	127. (1)	128. (4)	129. (3)	130. (1)
131. (1)	132. (2)	133. (2)	134. (2)	135. (4)
136. (3)	137. (4)	138. (3)	139. (4)	140. (3)
141. (1)	142. (2)	143. (1)	144. (3)	145. (4)
146. (2)	147. (1)	148. (1)	149. (4)	150. (4)
151. (2)	152. (2)	153. (3)	154. (1)	155. (4)
156. (1)	157. (4)	158. (1)	159. (1)	160. (4)
161. (4)	162. (1)	163. (2)	164. (4)	165. (2)
166. (1)	167. (2)	168. (1)	169. (1)	170. (1)

Multiple Correct Answers Type

1. (1, 2)	2. (1, 2, 4)	3. (1, 3, 4)
4. (1, 2, 3, 4)	5. (1, 3)	6. (1, 2)
7. (2, 4)	8. (1, 2)	9. (2, 4)
10. (1, 3)	11. (1, 4)	12. (1, 2, 3)
13. (3)	14. (1, 3, 4)	15. (1, 4)
16. (1, 2, 3)	17. (1, 2, 4)	18. (2, 3)
19. (2, 3, 4)	20. (1, 2, 4)	21. (1, 2)

22. (2, 4)	23. (2, 3)	24. (1, 2, 3)
25. (1, 3, 4)	26. (1, 4)	27. (2, 3, 4)
28. (3, 4)	29. (1, 2, 3, 4)	30. (1, 3, 4)
31. (2, 3)	32. (2, 3)	33. (1, 2, 3)

Linked Comprehension Type

1. (3)	2. (3)	3. (3)	4. (2,5)	5. (1,2)
6. (2)	7. (1)	8. (1)	9. (2)	10. (4)
11. (3)	12. (2)	13. (2)	14. (1)	15. (2)
16. (1)	17. (4)	18. (1)	19. (3)	20. (4)
21 (3)	22 . (1, 3	. 4)		

Matrix Match Type

Q.No.	a	b	c	d	9
1.	p, r	q, t	q, t	p, s	_
2.	р	q	r		_
3.	r	S	p	q	_
4.	р	q	r	S	_
5.	q	S	r	p	_
6.	ii, p	i, q	iv, r	v, t	iii, s
7.	ii, iv, q, r	i, iv, p, s	iii, q	v, t	

Numerical Value Type

1. (1)	2. (2)	3. (4)	4. (2)	5. (4)
6. (4)	7. (4)	8. (2)		

6. (4) 7. (4)

ARCHIVES

JEE Main

Single Correct Answer Type

		11		
1. (3)	2. (2)	3. (2)	4. (2)	5. (1)
6. (1)	7. (3)	8. (2)	9. (1)	10.
11. (4)	12. (4)	13 (3)		

JEE Advanced

Single Correct Answer Type

1. (1) Multiple Corr	3. (1)	4. (2)	5. (⁴⁾
1. (2, 3, 4)	2. (1, 2)	3. (2, 4)	

Numerical Value Type

1. (2)	2. (19)	3 , (0.05)

Electrochemistry

OVERVIEW

- 1. Electrochemical or galvanic or voltaic cell: It is a device in which chemical energy is converted into electrical energy. In this cell, a redox reaction is carried out in an indirect manner and the decrease in free energy during the chemical process appears as electrical energy.
 - The common galvanic cell, dry cell, and the lead storage battery are the devices for converting chemical energy into electrical energy.
- Daniell cell: It is a typical example of galvanic cell. It consists of two half cells, one containing Zn electrode in ZnSO₄(1 M) solution and the other containing Cu electrode in CuSO₄ (1 M) solution.
 - Zn electrode acts as anode and oxidation occurs at this electrode (Zn \longrightarrow Zn²⁺ + 2e⁻). Cu electrode acts as cathode and reduction occurs at this electrode (Cu²⁺ + 2e⁻ \longrightarrow Cu). When two half cells are connected with a salt bridge and electrodes are joined by a wire externally, electrons from Zn electrodes (negative electrode) move towards Cu electrodes (positive electrode), and the current flows from cathode to anode. The cell reaction is:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

- Salt bridge: It contains a paste of an inert electrolyte such as KCl, KNO₃, K₂SO₄, or NH₄NO₃ with agar-agar and gelatin. It allows the flow of current by completing the circuit and maintains electrical neutrality. It also prevents liquid-liquid junction potential.
- 4. Electrode potential: When a metal is placed in a solution of its ions, it acquires either a positive or negative charge with respect to the solution. On account of this a definite potential is developed between the metal and the solution. This potential difference is called *electrode potential*. It depends on the nature of electrode, concentration of ions, and temperature.
- 5. Oxidation potential: It is the tendency of an electrode to get oxidized, i.e., to lose electrons.

$$M \longrightarrow M^{n+} + ne^-$$

6. Reduction potential: It is the tendency of an electrode to get reduced, i.e., to accept electrons.

$$M^{n+} + ne^- \longrightarrow M$$

- 7. Standard electrode potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25°C (278 K) is called standard electrode potential.
- **8. EMF:** It is the difference in the potential across left and right electrodes due to which electrons flow from anode to cathode.
- 9. Standard EMF: The EMF values of an electrode under standard conditions (1 atm, 298 K) and the unit concentrations of its ions is called as standard EMF and is denoted by E^{\ominus}_{cell} .
- 10. Reference electrode: The potential of an individual half cell cannot be measured but the difference in the potential of two half cells can be measured experimentally. It is, therefore, necessary to couple the electrodes with another electrode whose potential is known. This electrode is termed as *reference electrode*.
- 11. SHE or NHE: A half cell called standard or normal hydrogen electrode as the reference electrode is assigned a zero potential at all temperatures corresponding to the equation:

$$\mathrm{H}^{\oplus}(\mathrm{aq}) + e^{-} \longrightarrow \frac{1}{2} \mathrm{H}_{2}(\mathrm{g})$$

It consists of a platinum electrode coated with platinum black dipped in acidic solution at unit concentration and H_2 gas at 1 atm pressure, and is bubbled through it at 298 K. This is termed as SHE or NHE. It is reversible with respect to H^\oplus ions. It is represented as

Pt(s) | H₂(g) (1 bar) | H[⊕](1 M)

$$E^{\ominus}_{H_2(g) \mid 2H^{\oplus}} = E^{\ominus}_{2H^{\oplus} \mid H_2(g)} = 0.0 \text{ V at } 298 \text{ K}$$

12. E^{\odot}_{cell} : In electrochemical cell, anode is the electrode with higher oxidation potential or lower reduction potential and cathode is vice-versa. Also.

a.
$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{red}})_{\text{cathode}} - (E^{\odot}_{\text{red}})_{\text{anode}}$$
or

b.
$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{oxid}})_{\text{anode}} - (E^{\odot}_{\text{oxid}})_{\text{cathode}}$$
or

c.
$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{oxid}} + E^{\odot}_{\text{red}}$$

- 13. Electrochemical series: When electrodes (metals or nonmetals) in contact with their ions are arranged on the basis of their standard reduction potential or standard oxidation potential, the resulting series is called the electrochemical series of the elements. It is used
 - a. To compare the relative activities of metals.
 - b. To compare relative oxidizing and reducing powers.
 - c. In the determination of pH of the solution, $K_{\rm sp}$, $K_{\rm eq}$, and for potentiometric titrations.

14. Cell diagrams and terminology

Consider a Daniell cell with the following cell reaction:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

	Anode	Cathode
Reaction	Oxidation takes place	Reduction takes place
Zı	$n(s) \to Zn^{2+}(aq) + 2e^{-}$	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Terminal	Negative	Positive
Side	LHS	RHS
Diagram	$Zn^{\odot} \mid Zn^{2+}(aq)$	Cu ²⁺ (aq) Cu

Complete cell diagram has a salt bridge, represented by a double vertical line (||).

 $Zn \mid Zn^{2+}(aq) \mid \mid Cu^{2+}(aq) \mid Cu$

- a. Electrodes are at the extreme corners.
- b. If the oxidized or reduced part is a gas, use Pt electrode saturated with that gas.

Thus, for anode (oxidation half cell) with reactions

i.
$$H_2(g) \longrightarrow 2H^{\oplus}(aq) + 2e^{-}$$

$$Pt(H_2) \mid H^{\oplus}(aq)$$

ii.
$$2Cl^{\odot}(aq) \longrightarrow Cl_2(aq) + 2e^{-}$$

$$Pt(Cl_2) \mid Cl^{\Theta}(aq)$$

For cathode (reduction half cell) with reactions

i.
$$2H^{\oplus}(aq) + 2e^{-} \longrightarrow H_{2}(g)$$

$$H^{\oplus}(aq) \mid Pt(H_2)$$

ii.
$$Cl_2(g) + 2e^- \longrightarrow 2Cl^{\Theta}(aq)$$

$$Cl^{\Theta}(aq) \mid Pt(Cl_2)$$

How to apply the terms cathode and anode to an electrolysis cell.

Regardless whether a cell is a voltaic or an electrolysis cell, the anode is the electrode at which reduction occurs. The cathode is the electrode at which reduction occurs.

	Voltaic cell	Electrolysis cell
Anode	Oxidation negative (-) terminal	Oxidation positive (+) terminal
Cathode	Reduction positive (+) terminal	Reduction negative (-) terminal

15. Electrical work, ΔG^{\odot} , and spontaneous change

 ΔG represents the maximum amount of useful work that a constant pressure process can perform.

$$\Delta G = -W_{\text{max}} \text{ (useful)}$$

a. For a spontaneous change, $\Delta G < 0$ and work done by the system is negative. When a reaction occurs in a voltaic

cell it does work, i.e., electrical work.

$$-W_{\text{electrical}} = -nFE_{\text{cell}}$$

$$\Delta G = -nFE_{\text{cell}}$$

- b. If reactants and products are in their standard states, $\Delta G^{\odot} = -nF\dot{E}^{\odot}_{cell}$
- c. If E_{cell} is positive, reactions occurs spontaneously in the forward direction.
- **d.** If E_{cell} is negative, reaction occurs spontaneously in the reverse direction.
- e. If a cell reaction is reversed, $E_{\rm cell}$ changes ${\rm sign}_{\rm L}$

16. Relationship between $E_{\mathrm{cell}}^{\ominus}$ and K_{eq}

 ΔG^{\odot} is related to thermodynamic equilibrium constant kby equation

$$\Delta G^{\odot} = -2.303RT \log K_{\text{eq}} \qquad ...(i)$$

$$\Delta G^{\odot} = -2.303RT \log K_{\text{eq}} = -nFE^{\odot}_{\text{cell}}$$

$$\therefore E^{\odot}_{\text{cell}} = \frac{2.303RT}{nF} \log K_{\text{eq}}$$

In standard state, at 25°C,

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.12 \text{ K}}{96500 \text{ C}}$$

$$\therefore E^{\odot}_{\text{cell}} = \frac{0.0591}{n} \log K_{\text{eq}} \qquad \dots \text{(ii)}$$

17. Relation between standard potentials of half cells containing a metal in different oxidation states: If two half reactions having potentials E^{\ominus}_{1} and E^{\ominus}_{2} are combined to give a half reaction having a potential E^{Θ}_{3} , then

$$\Delta G_3^{\ominus} = \Delta G_1^{\ominus} + \Delta G_2^{\ominus}$$

$$-n_3 F E_3^{\odot} = -n_1 F E_1^{\odot} - n_2 F E_2^{\odot}$$

$$n_3 E_3^{\odot} = n_1 E_1^{\odot} + n_2 E_2^{\odot}$$

$$E_3^{\odot} = \frac{n_1 E_1^{\odot} + n_2 E_2^{\odot}}{n_3} \qquad ...(i)$$

If equal number of electrons are involved, then

$$E_3^{\ominus} = E_1^{\ominus} + E_2^{\ominus} \qquad \dots (ii)$$

18. Nernst equation

For the reaction $aA + bB \longrightarrow cC + dD$

Reaction quotient
$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
 ...(i)

...(ii)

and
$$\Delta G = \Delta G^{\odot} + 2.303RT \log K$$

also
$$\Delta G = -nFE_{\text{cell}}$$
 $\Delta G^{\odot} = -$

Hence,
$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^{\odot} + 2.303RT \log K$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{2.303RT}{nF} \log K \qquad ...(iii)$$

This is called Nernst equation.

At 25°C,
$$\frac{2.303RT}{F} = 0.0591$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.0591}{1000} \log K \qquad ...(jv)$$

Here, n is the number of mol of electrons exchanged.

19. Concentration cells and liquid junction potential: In a cell if two electrons. if two electrolytic solutions of different concentrations are in contact with each other, a potential difference develops in contact develops develops the boundary of two solutions. It is called liquid junction potential or diffusion potential.

- Liquid junction potential is minimized in concentration cells (described below).
- . Salt bridge is placed between two half cells. This salt bridge contains agar-agar paste with NH₄NO₃, KNO₃, or KCl as conducting electrolytes. KCl is not used when electrode is made of Ag.
- . If salt bridge is removed, the potential falls to zero.

$_{20.~a.}$ Concentration cell in which electrode is reversible with respect to cation (electrolytic concentration cell)

$$Z_n \mid Z_n^{2+}(c_1) \parallel Z_n^{2+}(c_2) \mid Z_n$$

At LHS half cell

$$Zn \longrightarrow Zn^{2+}(c_1) + 2e^-; E^{\odot}_{oxid} = 0.76 \text{ V}$$

At RHS half cell:

$$Zn^{2+}(c_2) + 2e^- \longrightarrow Zn; E_{red}^{\ominus} = -0.76 \text{ V}$$

Net reaction: $Zn^{2+}(c_2) \longrightarrow Zn^{2+}(c_1)$; $E^{\Theta}_{Cell} = -0.00 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.0591}{2} \log \left(\frac{c_1}{c_2} \right) \left[\text{For concentration cell, } E_{\text{cell}}^{\odot} = 0 \right]$$
$$= \frac{0.0591}{2} \log \frac{c_2}{c_2}$$

Cell reaction is spontaneous or exergonic ($\Delta G = -ve$) in forward direction if

$$[Zn^{2+}]_{RHS}(c_2) > [Zn^{2+}]_{LHS}(c_1)$$

b. Concentration cell in which electrode is reversible with respect to anion

 $\mathsf{Pt}, \mathsf{Cl}_2(\mathsf{g})(\mathsf{1} \mathsf{\ atm}) \mid \mathsf{Cl}^{\scriptscriptstyle \bigcirc}(c_1) \parallel \mathsf{Cl}^{\scriptscriptstyle \bigcirc}(c_2) \mid \mathsf{Cl}_2(\mathsf{g})(\mathsf{1} \mathsf{\ atm}), \, \mathsf{Pt}$

$$E_{\text{cell}} = -\frac{0.059}{1} \log \left[\frac{c_2}{c_1} \right]$$

For such cases, cell reaction is spontaneous or exergonic $(\Delta G = -ve)$ in forward direction if $c_1 > c_2$.

c. Pt, $H_2(g)$ (1 atm) | $H^{\oplus}(c_1) \parallel H^{\oplus}(c_2) \mid H_2(g)$ (1 atm), Pt

$$E_{\text{cell}} = -\frac{0.059}{2} \log \left[\frac{H^{\oplus}(c_1)}{H^{\oplus}(c_2)} \right]^2$$

 E_{cell} is positive, when $c_2 > c_1$ or $pH_a > pH_c$ and $\Delta G = -ve$.

That is, the cell is exergonic or spontaneous.

21. Electrode concentration cell: In these cells, identical electrodes at different concentrations are dipped in the same solution of the electrolyte.

For example:

(i) Pt,
$$H_2(g)(p_1)$$
 | HCl (1 M) | $H_2(g)(p_2)$, Pt
$$E_{cell} = E_{cell}^{\ominus} - \frac{0.059}{2} \log \frac{p_2}{p_1}$$

$$= 0 - \frac{0.059}{2} \cdot p_2$$

$$= 0 - \frac{0.059}{2} \log \frac{p_2}{p_1}$$

 $E_{\text{cell is positive, if } p_1 > p_2}$ and the cell is spontaneous or feasible or exergonic ($\Delta G = -\text{ve}$).

For example,

(ii) Pt, $\operatorname{Cl}_2(g)(p_1) \mid \operatorname{Cl}^{\odot}(1 \text{ M}) \mid \operatorname{Cl}_2(g), (p_2), \operatorname{Pt}$

 E_{cell} is positive, if $p_2 > p_1$ and cell is spontaneous or feasible or exergonic ($\Delta G = -\text{ve}$).

Concentration cell formed by coupling the electrolytic concentration cell and electrode concentration cell.

For example,

Pt, H₂(
$$p_1$$
 atm) | H ^{\oplus} (M_1) || H ^{\oplus} (M_2) | H₂ (p_2 atm), Pt

$$E_{\text{cell}} = -\frac{0.059}{2} \log \frac{(p_2)_c [H^{\oplus}(M_1)]_a^2}{(p_1)_a [H^{\oplus}(M_2)]_c^2}$$

$$= -0.059 \left[(pH_c - pH_a) - \frac{1}{2} \log \frac{(p_2)_c}{(p_1)_a} \right]$$

$$= 0.059 \left[(pH_a - pH_c) + \frac{1}{2} \log \frac{(p_1)_a}{(p_2)_c} \right]$$

22. Determination of thermodynamic data

a.
$$\Delta G = -nFE_{\text{cell}}$$

Using Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T \left(\frac{d(\Delta G)}{dT} \right)_P$$
 ...(i)

$$-nFE_{\text{cell}} = \Delta H - nFT \left(\frac{dE_{\text{cell}}}{dT} \right)_{P}$$

Temperature coefficient of the EMF of the cell can be determined.

$$\left(\frac{dE_{\text{cell}}}{dT}\right)_P = \frac{\Delta H + nFE_{\text{cell}}}{nFT}$$

$$\left(\frac{dE_{\text{cell}}}{dT}\right)_P = \frac{\Delta H}{nFT} + \frac{E_{\text{cell}}}{T}$$

b. Enthalpy change can be determined.

$$\Delta H = -nFE_{\text{cell}} + nFT \left(\frac{dE_{\text{cell}}}{dT} \right)_{P}$$
$$= -nF \left[E_{\text{cell}} - T \left(\frac{dE_{\text{cell}}}{dT} \right)_{P} \right]$$

Entropy change can be determined.

$$\Delta G = \Delta H - T \Delta S$$

Comparing the above equation with Eq. (i), we get

$$\Delta S = -\left(\frac{d(\Delta G)}{dT}\right)_{P}$$

$$= -\left(\frac{d}{dT}(-nFE_{\text{cell}})\right)_{P}$$

$$= nF\left(\frac{dE_{\text{cell}}}{dT}\right)_{P}$$

23. Determination of equilibrium constant

At equilibrium, $E_{\text{cell}} = 0.00 \text{ V}$

$$\therefore E^{\ominus}_{\text{cell}} = \frac{0.0591}{n_{\text{cell}}} \log K_{\text{eq}}$$

$$\log K_{\rm eq} = \frac{n_{\rm cell} \times E_{\rm cell}^{\odot}}{0.059}$$

Equilibrium constants involving complex ions have been evaluated, e.g., $Ag^{\oplus} + 2NH_3 \longrightarrow [Ag(NH_3)_2]^{\oplus}$

24. Determination of solubility product

a. Solubility products of sparingly soluble salts have been evaluated from EMF measurements. Suppose we want to determine $K_{\rm sp}$ of AgX(s). Its saturated solution is placed in Ag electrode in Ag $^{\oplus}$ ion.

Ag | Ag[®] saturated AgX(aq) || Ag[®] (c) | Ag Its E_{cell} is measured.

$$Ag \longrightarrow Ag^{\oplus}$$
 (in saturated AgX) + e^-

$$E_{\text{oxid}} = -0.80 \text{ V}$$

$$Ag^{\oplus}$$
 (in given solution, c) + $e^- \longrightarrow Ag$

$$E_{\text{red}}^{\odot} = +0.80 \text{ V}$$

$$Ag^{\oplus}(c) \longrightarrow Ag^{\oplus} (unknown)$$

$$E_{\text{cell}}^{\odot} = 0.00 \text{ V}$$

$$K = \frac{[Ag^{\oplus}(unknown)]}{[Ag^{\oplus}(c)]}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - 0.0591 \log \frac{[Ag^{\oplus}]}{c}$$

$$= 0 + 0.0591 \log \frac{c}{[Ag^{\oplus}]}$$

Hence, [Ag[⊕]] in LHS is evaluated.

Thus,
$$K_{\rm sp} = [Ag^{\oplus}][X^{\odot}] = [Ag^{\oplus}]^2$$

b. If E^{\odot} of X^{\odot} | AgX, Ag (half cell) is given then $K_{\text{sp}} \circ f_{\text{AgX}}$ can be evaluated using equation

$$\frac{0.0591}{n} \log K_{\text{sp}} = E^{\odot}_{(X^{\bigcirc} \mid AgX, Ag)} - E^{\odot}_{(Ag^{\bigoplus} \mid Ag)}$$
$$= E^{\odot}_{(X^{\bigcirc} \mid AgX, Ag)} + E^{\odot}_{(Ag \mid Ag^{\bigoplus})} ...[i]$$

$$Ag(s) \longrightarrow Ag^{\oplus}(aq) + e^{-} \qquad E^{\ominus}_{ox}$$

$$\frac{\operatorname{AgX}(s) + e^{-} \to \operatorname{Ag}(s) + X^{\odot}(aq)}{\operatorname{AgX}(s) \longrightarrow \operatorname{Ag}^{\oplus} + X^{\odot}(aq)} = E^{\odot}_{\text{red}} = E^{\odot}_{(X^{\odot}|A_{g}X_{Ag})}$$

$$\frac{\operatorname{AgX}(s) \longrightarrow \operatorname{Ag}^{\circ} + \operatorname{A}^{\circ}(\operatorname{aq})}{E^{\circ}_{\operatorname{cell}} = E^{\circ}_{(\operatorname{Ag} \mid \operatorname{Ag}^{\oplus})} + E^{\circ}_{(\operatorname{X}^{\circ} \mid \operatorname{AgX}, \operatorname{Ag})}$$

$$K_{\rm eq}[Ag^{\oplus}][X^{\odot}]$$

$$E_{\text{cell}} = 0.00 \text{ V}$$

= $E_{\text{cell}}^{\odot} - \frac{0.0591}{1} \log K_{\text{sp}}$

$$\therefore E^{\odot}_{\text{cell}} = 0.0591 \log K_{\text{sp}}$$

:.
$$E^{\ominus}_{(Ag \mid Ag^{\oplus})} + E_{(X^{\ominus} \mid AgX,Ag)} = 0.0591 \log K_{sp}$$

Note: Equation (i) is to be used when a half cell contains electrolyte in saturated solution.

25. Various types of half cells

S. No. Type	Example	Reduction half cell reaction	Reversible to	$E_{ m cell}$
Metal-metal in half cell	$Ag^{\oplus}(aq) Ag(s)$	$Ag^{\oplus}(aq) + e^{-} \longrightarrow Ag(s)$	Ag [⊕] ion	$E = E^{\odot}_{\text{cell}} - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^{\odot}]}$
2. Gas-ion half cell	$H^{\oplus}(aq) H_2(g)$ (1 atm), Pt	$H^{\oplus}(aq) + e^{-} \longrightarrow \frac{1}{2} H_2(g)$ (1 atm)	H [⊕] ion	$E = 0 - \frac{0.059}{1} \log \frac{1}{[H^{\oplus}]}$ or $E_{H_2} = -0.059 \text{ pH}$
	Cl [⊙] (aq) Cl ₂ (g) (1 atm), Pt	$\frac{1}{2}\operatorname{Cl}_2(g) + e^- \longrightarrow \operatorname{Cl}^{\Theta}(\operatorname{aq})$	Cl [⊖] ion	$E = E^{\odot} - 0.059 \log \left[\text{Cl}^{\odot} \right]$
3. Metal-insoluble salt anion half cell	Cl [⊕] (aq) AgCl(s), Ag	$AgCl(s) + e^- \rightarrow Ag + Cl^{\Theta}(aq)$	Cl [⊖] ion	$E = E^{\odot} - 0.059 \log \left[\text{Cl}^{\odot} \right]$
4. Calomel electrode half cell	$Cl^{\Theta}(aq) Hg_2Cl_2(s), Hg(l)$	$Hg_{2}Cl_{2}(s) + 2e^{-} \longrightarrow$ $2Hg(l) + 2Cl^{\Theta}(aq)$	Cl [⊙] ion	$E = E^{\odot} - \frac{0.059}{2} \log [\text{Cl}^{\odot}]^{2}$ $E_{\text{SCE}} = 0.24 V \text{ Refer}$ $E_{\text{NCE}} = 0.268 V \text{ Section}$ $E_{\text{DNCE}} = 0.338 \left[3.10(\text{c}) \right]$
5. Mercury-mercurous sulphate electrode (Hg-Hg ₂ SO ₄) half cell	$SO_4^{2-}(aq) Hg_2SO_4(s),$ Hg(1)	$Hg_{2}SO_{4}(s) + 2e^{-} \longrightarrow$ $2Hg(1) + SO_{4}^{2-}(aq)$	SO ₄ ²⁻ ion	$E = E^{\odot} - \frac{0.059}{2} \log[SO_4^{2^-}]$ $E^{\odot}_{red} = 0.616 \text{ V (w.r.t. SHE)}$

6. Mercury-mercuric	SO ₄ ²⁻ (aq) HgSO ₄ (s),Hg(l)		SO ₄ ²⁻ ion	$E = E^{\odot} - \frac{0.059}{2} \log[SO_4^{2-}]$
6. Mes sulphate (Hg-HgSO ₄)		$Hg(1) + SO_4^{2-}(aq)$		
half cell 7. Quinhydrone	H [⊕] (aq) Quinhydrone, Pt	$O = \langle$	H [⊕] ion	$E = E^{\odot} - \frac{0.059}{2} \log \frac{1}{[H^{\oplus}]^2}$
7. Quilling half cell		HO-\(\)\-OH \(\)		or
		$ \begin{array}{c} \text{Or} \\ \text{Q} + 2\text{H}^{\oplus} + 2e^{-} \longrightarrow \text{H}_{2}\text{Q} \end{array} $		$E = E^{\odot} - 0.059 \text{ pH}$ $E^{\odot}_{(Q,2H\oplus H_2Q)} \approx 0.7 \text{ V}$

Note: If it is combined with SCE to form a cell as:

Hg, Hg₂Cl₂(s), KCl (saturated solution)
$$\parallel$$
 H ^{\oplus} (x M) Q, QH₂ | Pt

$$\frac{\text{Hg, Hg, P}}{\text{E}_{(Q, 2\text{H}\oplus | \text{H}_2\text{Q})}} = \text{E}^{\ominus}_{(Q, 2\text{H}\oplus | \text{H}_2\text{Q})} - 0.059 \text{ pH} = 0.7 \text{ V} - 0.059 \text{ pH}$$

$$E_{SCE} = 0.24 \text{ V}$$

$$E_{\text{cell}} = E_{(Q,2H\oplus | H_2Q)} - E_{\text{SCE}} = (0.7 \text{ V} - 0.059 \text{ pH}) - (0.24 \text{ V})$$

$$\therefore pH = \frac{0.7 - 0.24 - E_{cell}}{0.059}$$

8. Metal-metal hydroxide half cell	[⊙] OH (aq)/HgO, Hg(l)	$\begin{array}{c} \text{HgO(s)} + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow \\ 2\text{OH (aq)} + \text{Hg(l)} \end{array}$	[⊙] OH ion	$E = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log[\text{OH}]^2$
9. Oxidation–reduction half cell	Fe ³⁺ , Fe ²⁺ Pt	$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$	Fe ²⁺ and Fe ³⁺ ion	$E = E^{\odot} - 0.059 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$
10. The glass electrode	0.1 M HCl; Pt Glass	$H^{\oplus}(aq) + e^- \longrightarrow \frac{1}{2} H_2(g)$	H [⊕] ion	$E_{\rm G} = E^{\odot}_{\rm G} - 0.059 \log \frac{1}{[{\rm H}^{\oplus}]}$ or $E_{\rm G} = E^{\odot}_{\rm G} - 0.059 {\rm pH}$
		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	wise (\$4" a Fig.	G G STOOP PLL

Note: If it is combined with SCE to form a cell as:

Pt, 0.1 M HCl | Glass | Experimental solution | KCl (saturated solution), Hg_2Cl_2 , Hg]; $E_{SCE} = 0.24 \text{ V}$

$$E_{cell} = E_{SCE} - E_{G}$$

= 0.24 V - (E^{\circ}_G - 0.059 pH)

$$\therefore \text{ pH} = \frac{E_{cell} - 0.24 + E^{\odot}_{G}}{0.059}$$

Ag—AgCl, Hg—H₂SO₄, Hg—HgSO₄ and calomel electrode are secondary reference electrodes.

26. Electrolysis

a. Electrolysis: Nonspontaneous chemical change

When a cell reaction in a voltaic cell is reversed by reversing the direction of the electron flow, the voltaic cell changes into an electrolysis cell. Thus, for a voltaic cell, if

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s);$$

$$E^{\odot}_{cell} = +1.10 \text{ V}$$

Then, for an electrolysis cell,

$$Zn^{2+}(aq) + Cu(s) \longrightarrow Zn(s) + Cu^{2+}(aq);$$

$$E_{\text{cell}}^{\Theta} = -1.10 \text{ V}$$

b. General rules of electrolysis of aqueous solutions using inert electrode (✓ indicates that the oxidation/reduction will occur and × indicates that the oxidation/reduction will not occur)

- i. (\checkmark) Reduction potential of $H_2O > (x)$ Reduction potential of cations of 1, 2, and 13 groups of periodic table, e.g., Na^{\oplus} , K^{\oplus} , Ca^{2+} , Mg^{2+} , Al^{3+} , etc. So reduction of H_2O occurs at cathode.
- ii. (x) Reduction potential of H₂O < (√) Reduction potential of other cations (than cations of 1, 2, and 13 group), e.g., Cu²⁺, Ag[⊕], Au³⁺, Cd²⁺, Zn²⁺, etc. So reduction of H₂O does not occur at cathode.

iii. (\checkmark) Oxidation potential of $H_2O > (*)$ oxidation potential of F[©], SO₃²⁻, SO₄²⁻, NO₃[©], S₂O₃²⁻, etc.

So oxidation of H₂O occurs at anode.

iv. (*) Oxidation potential of $H_2O < (\checkmark)$ oxidation potential of Cl[⊙], Br[⊙], I[⊙], etc.

So oxidation of these ions occurs at anode.

Note:

- i. Although the oxidation potential of $H_2O > oxidation$ potential of Clo, so H2O should get oxidized in preference to CI[©](aq). However on account of over potential of O₂, oxidation of Clo to Cl2 is preferred at anode
- ii. In electrolysis, cations move towards cathode and anions move towards anode and the "chance" of their deposition/liberation depends on their electrode potential, concentration, over potential, etc.
- c. Sign convention used in electrolysis: Regardless of whether a cell is a voltaic cell or an electrolysis cell,
 - The anode is the electrode at which oxidation takes place. It is the positive (+) terminal.
 - · The cathode is the electrode at which reduction takes place. It is the negative (-) terminal.
- d. Preferential discharge theory: If more than one type of ion is attracted towards a particular electrode, then the ion discharged is the one which requires least energy.

The decreasing order of the discharge potential or the increasing order of deposition for the cations and anions is as follows:

Cations: K^{\oplus} , Na^{\oplus} , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , H^{\oplus} , Cu^{2+} , Ag^{\oplus} ,

Anions: SO_4^{2-} , NO_3^{\ominus} , $\stackrel{\odot}{OH}$, Cl^{\ominus} , Br^{\ominus} , I^{\ominus}

e. Faraday's law of electrolysis

i. First law of electrolysis: The amount of chemical change produced is proportional to the quantity of electric charge passing through an electrolysis cell. Greater the number of mole of electrons transferred, the greater the mass of the products. An equivalent of a substance is associated with 1 mol of electrons in half reaction. Anode (oxidation):

$$\frac{1}{2}\,\mathrm{H}_2\mathrm{O} \longrightarrow \frac{1}{2}\mathrm{O}_2(\mathrm{g}) + \mathrm{H}^\oplus(\mathrm{aq}) + e^-$$

Cathode (reduction):

$$\frac{1}{2}\text{Cu}^{2+}(\text{aq}) + e^{-} \longrightarrow \frac{1}{2}\text{Cu}(\text{s})$$

From these half equations we would define one (electrochemical) equivalent as equal to 0.5 mol H₂O, 1 mol H^{\oplus} , 0.5 mol Cu^{2+} , and 0.5 mol Cu(s). Thus, the passage of 1 mol electrons through the electrolysis cell will deposit 0.5 mol of Cu at the cathode.

Current $(C/s) \times Time(s) = Charge(C)$

$$w = zIt = Zc$$

where w is the weight of the metal deposited/gag liberated due to passage of current I ampere for Interacted due to F liberated d defined by the equation.

$$Z = \frac{Aw}{\text{Electrons exchanged} \times 96500}$$

1 F = 96500 C

$$Ag^{\oplus} + e^{-} \longrightarrow Ag$$

$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

$$Al^{3+} + 3e^{-} \longrightarrow Al$$

Thus, 1 Faraday (96500 C) of electricity will produce 1 g equivalent each of Ag, Cu, and Al at cathode or 1 mol of Ag, 0.5 mol of Cu, and 0.33 mol of Al.

ii. Second law of electrolysis: A given quantity of electricity produces the same number of equivalents of any substance on electrolysis.

$$\left(\frac{\text{Weight of metal A}}{\text{Weight of metal B}} = \frac{\text{Equivalent weight of A}}{\text{Equivalent weight of B}}\right)$$

iii. Faraday's first and second law can be combined to give a mathematical relation as follows:

$$W = Zq = \frac{Ew}{F} \times Q = \frac{Q}{F} \times Ew$$
$$= \frac{Q}{F} \times \frac{Aw}{Z} = \frac{I \times t}{F} \times \frac{Aw}{z}$$

where z is valency of metal, w is the weight of substance deposited/liberated, Z is the electrochemical equivalent, Ew is equivalent weight, Aw is the atomic weight, I is the current, and t is time in seconds.

27. Corrosion

Corrosion is slowly coating the metallic surfaces with oxides or other salts of the metal. Corrosion of iron is called rusting In corrosion, a metal is oxidized by the loss of electrons to 02 and oxides are formed. It is a electrochemical phenomenon For example, at a particular spot of iron, oxidation occurs and that spot behaves as anode.

Anode:
$$2\text{Fe(s)} \longrightarrow 2\text{Fe}^{2+} + 4e^{-}; \ E_{(\text{Fe}^{2+}|\text{Fe})}^{\ominus} = -0.44 \text{ V}$$

Electrons released at anodic spot reduces O2 in presence of H[⊕] at another spot. The H[⊕] ions are obtained from H₂CO₃

$$(CO_2 + H_2O \longrightarrow H_2CO_3).$$

Cathode:
$$O_2(g) + 4H^{\oplus}(aq) + 4e^- \longrightarrow 2H_2O(l)$$

$$E^{\ominus}_{(H^{\oplus}|O_2|H_2O)} = 1.23^{\text{V}}$$

Overall reaction:

$$2\text{Fe(s)} + \text{O}_2(g) + 4\text{H}^{\oplus}(aq) \longrightarrow 2\text{Fe}^{2+}(aq) + 2\text{H}_2\text{O(l)}$$

$$E_{\text{cell}}^{\ominus} = 1.67^{\text{V}}$$

Fe²⁺ are further oxidized by atmospheric O_2 to form rust $(Fe_2O_3\cdot x H_2O)$.

(a) Atmospheric oxidation

$$2Fe^{2+}(aq) + 2H_2O(1) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^{\theta(\beta Q)}$$

(b) Prevention of corrosion

- i. By covering the surface of metal with paint or by
- ii. By covering the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object.
- iii. Sacrificial protection by more reactive metals (such as Mg, Zn, etc.) which corrode themselves but save the

28. Conductance of electrolytic solution

a. Resistance
$$(R) = \frac{\text{Potential difference } (E)}{\text{Current } (I)}$$

$$i.e.$$
, ohm (Ω) = $\frac{\text{Volts}}{\text{Amperes}}$

SI units of ohm = $(kg m^2)/(S^3A^2)$

b. Conductance
$$(G) = \frac{1}{R}$$

units = ohm⁻¹ or mho or siemens (S) or Ω^{-1} .

c. $R \propto \frac{l}{a}$ or $R = \rho \frac{l}{a}$, where l = length of the conductor, a =area of cross section of conductor, and ρ (rho) =

Units of $\rho = R \times \frac{a}{I} = \text{ohm-cm or ohm m in SI units.}$

(1 ohm-m = 100 ohm-cm)

resistivity (or specific resistance).

d. Cell constant: (G^*) (cm⁻¹ or m⁻¹) (SI units)

$$G^* = \frac{l}{a}$$

 $\therefore \kappa = \text{Conductance} \times \text{cell constant}$

$$\kappa = G \times G^* \text{ (ohm}^{-1} \text{ cm}^{-1} \text{ or S cm}^{-1} \text{ or S m}^{-1})$$

(SI units)

$$(1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1})$$

e. Specific conductance (or conductivity) κ (Kappa)

$$G = \frac{1}{R} = \frac{a}{\rho l}$$

$$G = \frac{1}{R} = \frac{a}{\rho l}$$
 (Since $R = \rho \frac{l}{a}$)

$$= \kappa \times \frac{a}{l}$$

$$\therefore \kappa = \frac{1}{\rho} = ohm^{-1} \text{ cm}^{-1} \text{ or S cm}^{-1} \text{ or S m}^{-1} \text{ (SI units)}$$

- f. Equivalent conductivity (Λ_{eq})
 - $\Lambda_{\rm eq}$ = Specific conductance (or conductivity) × ($V_{\rm solution}$ containing 1 g equivalent of electrolyte) $(\Lambda_{eq} = \kappa_v \times V)$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \text{ohm cm}^{-1} \times \frac{(\text{cm}^3 \text{ L}^{-1})}{(\text{gram equivalent L}^{-1})}$$
$$= \text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$
$$= \text{S cm}^2 \text{ eq}^{-1}$$

 $= S m^2 eq^{-1} (SI units)$

In terms of SI units:

$$\Lambda_{\text{eq}} (\text{S m}^2 \text{ eq}^{-1}) = \frac{\kappa (\text{S m}^{-1})}{N (\text{gram equivalent m}^{-3})}$$

Note: There is no multiplication with 1000.

$$(1 \text{ S m}^2 \text{ eq}^{-1} = 10^4 \text{ S cm}^2 \text{ eq}^{-1}).$$

- g. Molar conductivity (Λ_m)
 - $\Lambda_{\rm m} = {\rm Specific\ conductance\ (or\ conductivity)} \times (V_{\rm solution})$ containing 1 mol of electrolyte) $(\Lambda_m = \kappa_v \times V)$

or
$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M} = \text{ohm cm}^{-1} \times \frac{(\text{cm}^3 \text{ L}^{-1})}{(\text{mol L}^{-1})}$$

= ohm cm² mol⁻¹

 $= S cm^2 mol^{-1}$

 $= S m^2 mol^{-1} (SI units)$

$$(1 \text{ S m}^2 \text{ mol}^{-1} = 10^4 \text{ S cm}^2 \text{ mol}^{-1})$$

In terms of SI units:

$$\Lambda_{\rm m} ({\rm S} \ {\rm m}^2 \ {\rm mol}^{-1}) = \frac{\kappa ({\rm S} \ {\rm m}^{-1})}{M \ ({\rm mol} \ {\rm m}^{-3})}$$

Note: There is no multiplication with 1000.

h. Relation between $\Lambda_{\rm m}$ and $\Lambda_{\rm eq}$:

 $\Lambda_{\rm m} = \Lambda_{\rm eq} \times \text{Total charge of cation or anion}$

$$= \Lambda_{\text{eq}} \times n_{\oplus} \times Z_{\oplus} \text{ or } n_{\odot} \times Z_{\odot} = \Lambda_{\text{eq}} \times n_{\odot} \times Z_{\odot}$$

where n_{\oplus} and n_{\odot} are number of positive and negative charge. Z_{\oplus} and Z_{\odot} are the valency of positive and negative charges, respectively.

Alternatively:

$$\frac{\Lambda_{\rm eq}}{\Lambda_{\rm m}} = \frac{M}{N} = 'n' \text{ factor}$$

- i. Conductance (G), molar conductance (Λ_m) , and equivalent conductance (Λ_{eq}) increase with dilution whereas specific conductance (or conductivity) (κ) decreases with dilution.
- j. $\Lambda_{\rm m}^{\ \ c}$ (molar conductance of a strong electrolyte at concentration c) or Λ_{eq}^{c} (equivalent conductance of a strong electrolyte at concentration c) is given by **Debye–Huckel– Onsager equation:**

$$\Lambda_{\rm m}^{\ c} = \Lambda_{\rm m}^{\ \circ} - A\sqrt{c}$$

$$\Lambda_{\rm eq}^{\ c} = \Lambda_{\rm eq}^{\ o} - A\sqrt{c}$$

where A is the constant that depends upon the nature of solvent and temperature.

Thus, a plot of $\Lambda_{\rm m}$ versus \sqrt{c} is liner with slope = -A and intercept on y-axis is $\Lambda_{\rm m}^{\circ}$.

k. Kohlraush law of independent migration of ions: The molar conductivity of an electrolyte at infinite dilution (Λ_m°) is the sum of the ionic conductivities of cations and anions each multiplied with the number of ions present in one formula unit of the electrolyte. Mathematically,

$$\Lambda_{\rm m}^{\circ} (Ax By) = x\lambda_{(A^{+y})}^{\circ} + y\lambda_{(B^{-x})}^{\circ}$$

In terms of equivalent conductivities, it is defined as: The equivalent conductivity of an electrolyte at infinite dilution (Λ_{eq}°) is the sum of two values, one depending upon the cation and other upon the anion, i.e.,

$$\Lambda_{\rm eq}^{\circ}$$
 (Ax By) = $\lambda_{\rm (A^+y)}^{\circ} + \lambda_{\rm (B^-x)}^{\circ}$ where $\Lambda_{\rm eq}^{\circ}$ is the limiting equivalent (or ionic) conductivity of the electrolyte and $\lambda_{\rm c}^{\circ}$ and $\lambda_{\rm a}^{\circ}$ are the limiting equivalent (or ionic) conductivities of the cation and anion, respectively, at infinite dilution.

1. Degree of dissociation (α) of weak electrolyte at a concentration c is given by:

$$\alpha = \frac{{\Lambda_m}^c}{{\Lambda_m}^\circ} \text{ or } \frac{{\Lambda_{eq}}^c}{{\Lambda_{eq}}^\circ}$$

m. For sparingly soluble salts such as, AgCl, PbI₂, and CaSO₄, etc.

$$\Lambda_{\rm m}^{\ \circ} = \Lambda_{\rm m}^{\ c} = \frac{\kappa \times 1000}{M} = \frac{\kappa \times 1000}{S \text{ (solubility)}}$$

Hence,
$$S = \frac{\kappa \times 1000}{\Lambda_{\rm m}^{\circ}}$$

n. Calculation of dissociation constant $(K_a \text{ or } K_b)$ of weak electrolyte is given by:

$$K_{\rm a} = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\left(\Lambda_{\rm m}^{\ c}\right)^2}{\left(\Lambda_{\rm m}^{\ \circ}\right)^2 \left(1 - \frac{\Lambda_{\rm m}^{\ c}}{\Lambda_{\rm m}^{\ \circ}}\right)} = \frac{c\left(\Lambda_{\rm m}^{\ c}\right)^2}{\Lambda_{\rm m}^{\ \circ}\left(\Lambda_{\rm m}^{\ \circ} - \Lambda_{\rm m}^{\ c}\right)}$$

o. Determination of ionic product of water:

$$K_{\rm w} = [{\rm H}^{\oplus}] \ [\stackrel{\circ}{\rm OH}] = \left[\frac{\kappa \times 1000}{\Lambda_{\rm eq}^{0} \ ({\rm or} \ \Lambda_{\rm m}^{0})} \right]^{2}$$

p. Determination of degree of hydrolysis (h) of a salt of strong acid and weak base (S_A/W_B).

$$h = \frac{\kappa_1 - \kappa_2}{\kappa_3 - \kappa_2} = \frac{\Lambda_{m_1} - \Lambda_{m_2}}{\Lambda_{m_3} - \Lambda_{m_2}}$$

where Λ_{m1} is molar conductivity of the hydrolysed solution; Λ_{m2} is the molar conductivity of unhydrolyzed solution of concentration, c; and

 Λ_{m3} is the molar conductivity of, HCl solution of concentration c.

Knowing h, K_h (hydrolysis constant) can be determined.

$$K_{\rm h} = \frac{ch^2}{1 - h}$$

q. Abnormally high conductivities of H^{\oplus} and OH ions: H^{\oplus} ion has highest Λ_m at any temperature followed by OH. This is due to proton jump from one water molecule to another.

r. Effect of temperature and pressure on molar ionic conductivities:

It increases with increase of temperature (about $2\%_{per^{\circ}C}$ rise in temperature) and decreases with increase of pressure, because the viscosity of H_2O decreases with temperature and increases with pressure.

s. Transport or transference number: (t_{ion}) : The current flowing through an electrolyte solution is carried by ion_s . The fraction of current carried by an ion is called its transpon or transference number.

Transport number of cation (t_{\oplus})

$$= \frac{Current \ carried \ by \ cation}{Total \ current}$$

Transport number of anion (t_{\bigcirc})

$$= \frac{\text{Current carried by anion}}{\text{Total current}}$$

Thus, $t_{+} + t_{-} = 1$.

- t. Effect of concentration and temperature on transport number. With increase in concentration transport number decreases. Further, for (1:1) (uni-uni-valent) electrolyte, if t_{ion} is > 0.5, it decreases with increase of temperature till it approaches a value of 0.5.
 - i. t_{Cl} in HCl is less than that NaCl. Because t_{ion} α Speed of the ion

$$\therefore t_{\text{Cl}} = \frac{u_{\text{Cl}}}{u_{\text{H}} + u_{\text{Cl}}}$$

and
$$t_{\text{Cl}} = \frac{u_{\text{Cl}}}{u_{\text{Na}} + u_{\text{Cl}}}$$

(where μ_+ and μ_- are speed of cation and anions, respectively)

But
$$\mu_{H^{\bigoplus}}\!>\mu_{Na^{\bigoplus}}$$

because ${\rm H}^\oplus$ ion is much smaller in size than ${\rm Na}^\oplus$ ion] Hence, $t_{{\rm Cl}^\Theta}$ in ${\rm HCl}$ < $t_{{\rm Cl}^\Theta}$ in ${\rm NaCl}$.

ii.
$$t_{\text{Li}} \in t_{\text{Na}}$$
:

 Li^{\oplus} ion is smaller in size than Na^{\oplus} ion, so it should have greater transport number than Na^{\oplus} ion. But, experimentally, it is observed to be reverse.

This is because in solution Li[⊕] ion is much more hydrated than Na[⊕] ion. Hence, its speed becomes less and transport number of Li[⊕] becomes less than Na[⊕].

For the same reason, $t_{\text{Na}} \leftarrow t_{\text{K}} = \text{ion.}$

Etection

3.1 INTRODUCTION

Electrochemistry is the branch of chemistry that deals with the study of the production of electricity from chemical energy released during spontaneous redox reactions and the use of electrical energy to bring about non-spontaneous chemical transformation.

3.2 ELECTROCHEMICAL CELL

A device used to convert chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell or simply chemical cell. These are also called *galvanic cells* or *voltaic cells*, after the name of Luigi Galvani (1780) and Alessandro Volta (1800), respectively, who were the first to perform experiments on the conversion of chemical energy into electrical energy

Redox reaction between Zn and CuSO₄

The reaction is represented as:

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$
(or)

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

This reaction is splitted into two half reactions as follows:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$
 (oxidation half reaction)
 $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (Reduction half reaction)

The first reaction is called *oxidation half reactions* and the second is called the *reduction half reaction* and the reaction obtained by adding the two half reaction is called the overall reaction.

A zinc rod is placed in $ZnSO_4$ solution taken in a beaker. A copper rod is placed in $CuSO_4$ solution taken in another beaker.

Now, reaction takes place in either of the beakers and at the interface of the metal and its salt solution. In each beaker both the reduced and oxidized forms of the same species are present. These represent the species in the reduction and oxidation half reaction.

A redox couple is defined as having together the oxidized and reduced forms of a substance taking part in an oxidation or a reduction half reaction.

This is represented by separating the oxidized form from the reduced form by a vertical line or a slash representing an interface (e.g., solid/solution). For example, in this experiment the two redox couples are represented as Zn^{2+}/Zn and Cu^{2+}/Cu . In both the cases the oxidized form is put before the reduced from.

Now the two rods are connected by a wire and the two solution are connected by a *salf bridge* (Fig. 3.1). Thus provides an electric contact between the solutions without allowing them to mix with each other.

Salt bridge and its functions

It is a U-tube containing a solutions of an inert electrolyte such as, KCl, KNO₃, K₂SO₄, or NH₄NO₃ (ammonium nitrate) usually solidified by boiling with agar-agar and gelatin and later cooling to a jelly-like substance.

An inert electrolyte is one whose ions do not take part in the redox reaction and also do not react with the electrolyte used. The function of salt bridge is to allow the movement of ions from one solution to the other without mixing the two solutions. Thus, whereas the electrons flow is the outer circuit in the wire, the inner

circuit is completed by flow of ions from one solution to the other, through the salt bridge.

The main functions of salt bridge are:

- a. To complete the electrical circuit by flow of electrons in the outer circuit and by flow of ions from one solution to the other without mixing of the two solutions.
- **b.** To maintain the electrical neutrality of both the anodic and cathodic compartment.
- c. For the smooth flow of current, the electrolyte in the salt bridge should be such that the mobility or transport number of the cation of the electrolyte should be equal to the mobility of the anion of the electrolyte. For example, in KCl electrolyte mobility of K^{\oplus} ion = mobility of Cl^{\ominus} ion. Similarly in the KNO₃ electrolyte, mobility of K^{\oplus} ion = mobility of NO_3^{\ominus} ion.
- **d.** Also, it should not react with the contents of either cathode or anode. If the salt bridge is not used in the cell, the current stops flowing. This is explained as:
 - Electrons produced by zinc electrode flow toward the copper electrode and neutralizes some of the Cu²⁺ ions of the solution, leaving slightly greater concentration of SO₄²⁻ ions, and the solution acquires a negative charge. At the same time, Zn²⁺ ions produced from zinc rod enter into the ZnSO₄ solution and thus give it a positive charge. Due to the accumulation of charges in the two solutions, further flow of electrons will stop and hence the current stops flowing.
- e. Liquid junction potential: It also prevents liquid-liquid junction potential. When two electrolytic solutions are directly in contact, ions move across the junction with different speed. As a result, a potential difference is set up at the junction. It is called liquid junction potential (LJP). The EMF of cell is thus the sum of reduction potential of one electrode, oxidation potential of second electrode, and the liquid junction potential. Thus,

$$E = E_{\text{oxid}} + E_{\text{red}} + E_{j}$$

The salt bridge which contains the paste of KCl in which the mobility of K^{\oplus} and Cl^{\odot} ions are almost equal and hence E_i is taken as zero.

When salt bridge is used, the current flows continuously, since the accumulation of charges in the two solutions is simultaneously neutralized by the flow of opposite ions from the salt bridge into the two solutions.

The Zn and Cu rods are connected by a metallic wire with a provision for an ammeter/voltmeter and a switch. The setup, as shown in Fig. 3.1, is known as *Daniell cell*.

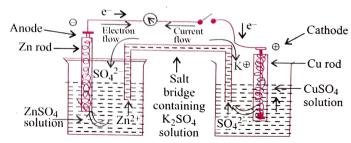


Fig. 3.1 Daniell cell having electrodes of Zn and Cu dipping in the solutions of their respective salts

When the switch is in the off position, no reaction takes place in either of the breakers and no current flows though the metallic wire. As soon as the switch is in the on position, the current flows through the metallic wire.

Some characteristics of the Daniell cell are as follows:

- a. The electrode at which oxidation takes place is called the anode (e.g., Zn electrode) and the electrode at which reduction takes place is called the cathode (e.g., Cu electrode).
- b. Anode is rich in electrons and forces these electrons into the external circuit and thus is designated as the *negative pole*. The cathode electrode requires electrons for the reduction of its ions into metal (i.e., Cu²⁺ ions into Cu). Thus, this electrode is deficient in electrons and withdraws electrons from the external circuit and therefore is designated as the *positive pole*.
- c. The electrons flow from the positive pole to the negative pole in the external circuit but conventionally the flow of current is represented in the opposite direction.
- d. Due to oxidation of metal into its ions (e.g., Zn to Zn²⁺ ions) at anode, the concentration of ions (Zn²⁺ ion) increases in the anode solution. Similarly, the reduction of ions to metals (e.g., Cu²⁺ to Cu) at cathode, the concentration of Cu²⁺ decreases and that of SO₄²⁻ ions increases in the cathode solution.

Thus, the electrical neutrality is maintained in both the anodic and cathodic compartments by flow of opposite ions from the salt bridge, which completes the inner circuit as shown in Fig. 3.1.

- e. During the operation of cell, Zn dissolves to give Zn²⁺ ions. The weight of anode electrode (i.e., Zn) decreases, whereas the weight of cathode electrode (i.e., Cu) increases due to the reduction of Cu²⁺ ion to Cu and deposition of Cu on cathode.
- f. But note that the loss in the weight of Zn electrode is not equal to the gain in the weight of Cu electrode. But loss in the gram equivalent of Zn is equal to the gain in the gram equivalent of Cu.
- g. Daniell cell converts chemical energy liberated during the redox reaction to electrical energy and has an electrical potential equal to 1.1 V when the concentration or activity of Zn²⁺ and Cu²⁺ ions is unity (1 mol dm⁻³).

$$Zn(s)+Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq)+Cu(s)$$

Note: In a dilute solution, activity is equal to concentration. Such a device is called a *galvanic* or a *voltaic* cell.

3.2.1 PORTABLE DANIELL CELL

Daniell cell with salt bridge is not portable so a portable and popular form of the cell is made in which salt bridge is replaced by a porous pot. In this cell, SO_4^{2-} ions migrate from $CuSO_4$ solution

to the $ZnSO_4$ solution to maintain the electrical neutrality in both anodic and cathodic compartments. The migration of $SO_4^{2-10\eta_8}$ from $CuSO_4$ solution is due to higher concentration of $CuSO_4^{4-10\eta_8}$ that of $ZnSO_4$ solution (Fig. 3.2).

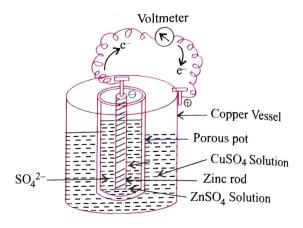


Fig. 3.2 Daniell cell

Another example of an electrochemical cell showing $red_{0\chi}$ reaction between Cu and AgNO₃ is given below.

The reaction is represented as:

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)(aq) + 2Ag(s)$$

 $Cu(s) + 2Ag^{\oplus}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

The two half reactions are:

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$$

(oxidation half reaction)

$$\frac{2Ag^{\oplus}(aq) + 2e^{-} \longrightarrow 2Ag(s) \quad \text{(reduction half reaction)}}{Cu(s) + 2Ag^{\oplus}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s) \text{ (cell reaction)}}$$

The cell is as shown in Fig. 3.3.

In this cell oxidation occurs at Cu electrode and hence it acts as anode or negative pole. Reduction occurs at Ag electrode and hence it acts as cathode or positive pole. The current flows conventionally from Ag to Cu.

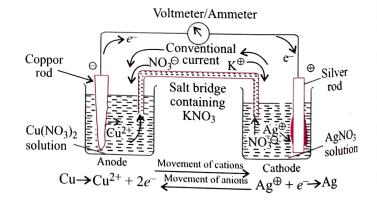


Fig. 3.3 Electrochemical cell based on the reaction

$$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$$

3.2.2 GALVANIC CELL

Galvanic cell is an electrochemical cell that converts chemical energy of a spontaneous redox reaction into electrical energy. In such device the Gibbs energy (G) of a spontaneous redox reaction

is converted into electrical work which may be used for running a motor or other electrical gadgets such as heater, fan, geyser, etc.

Some important characteristics of galvanic cells are as

follows:

- a. At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged.
- b. At the same time, metal atoms of the electrode have a tendency to go into solution as ions and leave behind the electrons at the electrode trying to make it negatively charged.
- c. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution.
- d. A potential difference develops between the electrode and the electrolyte which is called electrode potential. If the tendency of an electrode is to get oxidized, i.e., to lose electrons it is called oxidation potential and if the tendency of an electrode is to get reduced, i.e., to accept electrons, it is called reduction potential.
- e. When the concentration of all species involved in a half cell is unity, then the electrode potential is known as standard electrode potential and according to the "IUPAC convention," they are now called as standard reduction potential, i.e., at standard conditions (1 atm, 298 K, and 1.0 M).
- f. There exists a potential difference between the two electrodes and when a cell is in the "switch on" position, the electrons flow from negative electrode to positive electrode.
- g. The direction of current flow is opposite to that of electron flow.
- h. The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.

The cell potential is the difference between the reduction electrode potential of cathode and anode. It is called cell electromotive force (emf or EMF) of the cell when no current is drawn through the cell.

The efficiency of a cell is determined by the tendency of left electrode to loose electrons and the tendency of right electrode to accept electrons. Thus, a measure of cell efficiency is called as electromotive force (EMF) or the voltage or difference in potentials of two electrodes. EMF is defined as the difference in the potential across left and right electrode due to which electrons flow from anode to cathode

i. The EMF value of a cell made up of such two half cells is a constant provided that the concentration of the electrolyte, temperature, and pressure (if gases are involved) remains constant. It means that EMF values do not change with temperature, concentration and pressure. EMF values are hence standardized at a temperature of 25°C (298 K), a pressure of 1 atm or 1 bar (if gases are involved) and at concentrations of 1.0 M for all solutes present as electrolytes. EMF values under these condition are called as standard EMF and is denoted as E^{\odot} .

 E^{\odot}_{cell} can be defined in three ways as:

$$E^{\odot}_{\text{cell}}$$
 can be defined in three ways as:
i. $E^{\odot}_{\text{cell}} = \begin{cases} \text{Standard reduction potential of cathode} \\ - \text{Standard reduction potential of anode} \end{cases}$

$$= (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$$

ii.
$$E^{\ominus}_{\text{cell}} = \begin{cases} \text{Standard oxidation potential of anode} \\ - \text{Standard oxidation potential of cathode} \end{cases}$$

$$= (E^{\ominus}_{\text{oxidation}})_{\text{anode}} - (E^{\ominus}_{\text{oxidation}})_{\text{cathode}}$$

iii.
$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{oxidation}} + E^{\odot}_{\text{reduction}}$$

- j. Conventionally, anode is on the left and cathode is on the right while representing the galvanic cell.
- k. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge.

3.3 STANDARD HYDROGEN **ELECTRODE (SHE) AND** MEASUREMENT OF ELECTRODE **POTENTIAL**

The potential of individual half cell cannot be measured but the difference between the two half cell potentials that gives the EMF of cell can be measured. If the potential of one electrode (half cell) is chosen arbitrarily, then the potential of other half cell can be determined with respect to this. Conventionally, a half cell called standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) is taken as the reference electrode (Fig. 3.4) and represented as:

$$Pt(s) \mid H_2(g) \mid H^{\oplus}(aq),$$

is assigned a zero potential at all temperatures corresponding to the equation

$$H^{\oplus}(aq) + e^{-} \longrightarrow \frac{1}{2}H_{2}(g)$$

SHE consists of a platinum electrode coated with platinum black (finely divided platinum) dipped in an acidic solution and pure H₂ gas is bubbled through it.

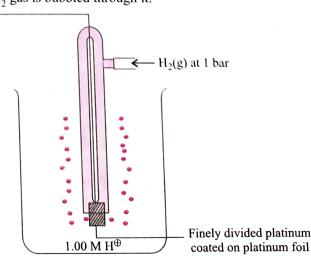


Fig. 3.4 Standard hydrogen electrode (SHE)

The concentration of both reduced and oxidized forms of hydrogen is maintained at unity, i.e., pressure of H_2 gas is 1 bar and concentration of H^{\oplus} ion in the solution is 1 M.

When, in the cell, this electrode acts as the cathode, i.e., reduction takes place, the following reaction occurs:

$$2H^{\oplus} + 2e^{-} \longrightarrow H_2(g)$$

i.e., some H^{\oplus} ions from the solution change into H_2 gas. When, in the cell, this electrode acts as the anode, i.e., oxidation takes place, the following reaction occurs:

$$H_2(g) \longrightarrow 2H^{\oplus} + 2e^{-}$$

or

i.e., some H_2 gas changes into H^\oplus ions which go into the solution. Thus, the electrode is reversible with respect to H^\oplus ions. The electrode is represented as:

$$Pt(s) \mid H(g) \mid 1 \text{ bar } \mid H^{\oplus} (1 \text{ M})$$

(where M is the concentration of H^{\oplus} ions)

$$E_{\text{H}_2(g) \mid 2\text{H}}^{\odot} = 0.0 \text{ V at } 298 \text{ K}$$

 $E_{\text{H}_2(g)}^{\odot} = 0.00 \text{ V at } 298 \text{ K}$

3.3.1 DETERMINATION OF ELECTRODE POTENTIAL OF AN ELECTRODE

A cell is set up using SHE as one of the electrodes and the second electrode is the electrode whose standard potential is to be determined. e.g., M^{S^+} M. The standard EMF of the cell is measured.

$$\begin{split} E^{\ominus}_{\text{cell}} &= (E^{\ominus}_{\text{reduction}})_{\text{cathode}} - (E^{\ominus}_{\text{reduction}})_{\text{anode}} \\ \text{If } E^{\ominus}_{(\text{M}^{+_{\mathcal{X}}} \mid \text{M})} &> E^{\ominus}_{2\text{H}^{\bigoplus} \mid \text{H}_{2}(\text{g})}, \end{split}$$

So $M^{+x} \mid M$ is the cathode and $H_2 \mid 2H^{\oplus}$ is the anode.

 $[\because$ Electrode having higher reduction potential has to be cathode]

Cell is represented as:

$$Pt(s) \mid H_2(g) \mid H^{\oplus} \parallel M^{x+} \mid M(s)$$

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{cathode}} - E^{\odot}_{\text{anode}}$$

$$x \text{ volt} = E_{\text{cathode}}^{\odot} - 0.0 \text{ volt } (E_{\text{SHE}}^{\odot} = 0.0 \text{ volt})$$

$$E^{\ominus}_{\mathbf{M}^{x+}/\mathbf{M}(\mathbf{s})} = x \text{ volt}$$

Thus, standard EMF of the cell will directly give the standard reduction potential of the electrode under investigation.

If
$$E^{\ominus}_{(M^{\alpha^+}/M)} < E^{\ominus}_{2H} \oplus_{/H_2(g)}$$

So M/M^{x^+} is the anode and $2H^{\oplus}/H_2$ is the cathode.

Then, the cell is represented as:

$$M(s) | M^{x+} || H^{\oplus} | H_2(g) | Pt$$

$$E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus}$$

$$x_{\text{volt}} = 0.0 \text{ volt} - E^{\odot}_{\text{anode}}$$

$$E^{\Theta}_{M^{+x}/M(s)} = -x \text{ volt}$$

Thus, standard EMF of the cell also directly gives the standard reduction potential of the electrode under investigation.

Moreover, the direction of the flow of current further indicates whether oxidation or reduction takes place on the electrode under investigation with respect to hydrogen electrode. Accordingly, the

electrode potential is termed as oxidation potential or $red_{uctio_{\eta}}$

Note:

- a. A reading on the voltmeter will be obtained only if the negative terminal of the voltmeter is connected to the negative electrode, i.e., where oxidation occurs and the positive terminal to the positive electrode, i.e., where reduction occurs.
- **b.** If the two half cells are selected arbitrarily for the purpose of constructing a galvanic cell, then proceed in the following manner:

Compare the reduction potentials of two electrodes. The electrode whose reduction potential has greater positive value is made cathode and other electrode is made anode. Alternatively, compare the oxidation potentials of two electrodes. The electrode whose oxidation potential has greater positive value is made anode and the other electrode is made cathode.

Constructing the cell in this manner will always give a positive EMF otherwise sometimes if electrode is chosen wrongly, the EMF will be negative. In such cases, if the EMF of the cell is positive, the cell is said to be spontaneous or feasible or exergonic ($\Delta G < 0$). If the EMF of the cell is negative, the cell is said to nonspontaneous or non-feasible or endergonic ($\Delta G > 0$).

c. Reduction potential is taken as standard potential, i.e., if electrode potential is given (and nothing is mentioned whether it is oxidation or reduction), it is taken as the reduction potential, by default.

3.3.2 RULES FOR ASSIGNING POSITIVE OR NEGATIVE SIGN TO ELECTRODE POTENTIALS

- a. The reduction potential of a half cell (or an electrode) is given a positive sign if the electrode acts as cathode in a cell arrangement with SHE and its oxidation potential is given a negative sign with the same magnitude.
 - For example: reduction potential of less active metals such as, Cu, Ag, etc., is given a positive sign.
- b. The oxidation potential of a half cell (or an electrode) is given a positive sign if the given electrode acts as anode in a cell arrangement with SHE and its reduction potential is given a negative sign with the same magnitude.

For example: Oxidation potential of active metals such as Na, K, Ca, Mg, Al, Zn, etc., is given a positive sign.

Note: Electrode potential measured in this manner is called as standard hydrogen scale potential.

A positive values of the standard electrode potential for $^{\text{Cu}}$ electrode indicates that $^{\text{Cu}^{2+}}$ ions gets reduced more easily than H^{\oplus} ions under the standard conditions. Alternatively, $^{\text{Cu}}$ cannot be oxidized to $^{\text{Cu}^{2+}}$ ions in presence of H^{\oplus} ions.

Hence Cu does not dissolve in HCl, whereas in case of H^{NO_3} (nitric acid), Cu is oxidized by NO_3^{\odot} (nitrate) ions and not by H^{\oplus} ions.

3.4 DIFFERENCE BETWEEN POTENTIAL DIFFERENCE AND EMF

potential difference and EMF of a cell differ as given below:

Potential difference	EMF
a. It is the difference between the electrode potentials of the two electrode under any condition. b. It is less than the maximum voltage obtainable from the cell (i.e., EMF of the cell).	 a. It is the potential difference between the two electrodes of the cell when no current is flowing in the circuit (i.e., in an open circuit). b. It is the maximum voltage obtainable from the cell.

 c. It is measured by a simple voltmeter. d. It is not responsible for the flow of steady current in the circuit. 	 c. It is measured by potentiommetric method only (given below), so that the EMF sent by the potentiometric source is equal and opposite to that of the cell and there is no net current flowing in the circuit. It cannot be measured by voltmeter which draws current. d. It is responsible for the flow of steady current in the circuit

3.5 MEASUREMENT OF EMF BY POTENTIOMETER METHOD

The EMF of a cell cannot be measured by a voltmeter because it withdraws some current from the cell and the equilibrium conditions are disturbed thereby. A potentiometer is used for this purpose.

3.6 ELECTROCHEMICAL SERIES

The standard electrode potentials are important and a lot of useful informations can be obtained from them. The values of standard electrode potential for some selected half cell reactions are given in Table 3.1.

JIC	3.1 Electrochemical se	Electrode reaction	Reduction potentials (V)	
	Li [⊕] /Li	$Li^{\oplus}(aq) + e^{-} \longrightarrow Li(s)$	-3.04	
	K [⊕] /K	$K^{\oplus}(aq) + e^- \longrightarrow K(s)$	-2.93	
	Ca ²⁺ /Ca	$Ca^{2+}(aq) + 2e^{-} \longrightarrow Ca(s)$	-2.87	
	Na [⊕] /Na	$Na^{\oplus}(aq) + e^{-} \longrightarrow Na(s)$	-2.71	
	Mg^{2+}/Mg	$Mg^{2+}(aq) + 2e^{-} \longrightarrow Mg(s)$	-2.37	
	Pt, H_2/H^{\oplus}	$H_2(aq) + 2e^- \longrightarrow 2H^{\oplus}(aq)$	- 2.25	
	Al^{3+}/Al	$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$	- 1.66	
	Mn ²⁺ /Mn	$Mn^{2+}(aq) + 2e^{-} \longrightarrow Mn(s)$	- 0.91	
	[⊙] OH /H ₂ , Pt	$2H_2O(1) + 2e^- \longrightarrow H_2(g) + 2OH (aq)$	- 0.83	
	Zn^{2+}/Zn	$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	- 0.76	es
Oxidising power increases	Cr ³⁺ /Cr	$Cr^{3+}(aq) + 3e^{-} \longrightarrow Cr(s)$	- 0.74	reas
	Fe ²⁺ /Fe	$Fe^{2+}(aq) + 2e^{-} \longrightarrow Fe(s)$	- 0.44	inc
	Cr^{3+}/Cr^{2+} , Pt	$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	-0.41	wer
	Cd ²⁺ /Cd	$Cd^{2+}(aq) + 2e^{-} \longrightarrow Cd(s)$	- 0.40	2 po
	Co ²⁺ /Co	$Co^{2+}(aq) + 2e^{-} \longrightarrow Co(s)$	-0.28	cing
	Ni ²⁺ /Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.25	Reducing power increases
Š	I [⊝] /AgI/Ag	$AgI(aq) + e^{-} \longrightarrow Ag(s) + I^{\odot}(aq)$	- 0.15	1
	Sn ²⁺ /Sn	$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \longrightarrow \operatorname{Sn}(\operatorname{s})$	- 0.14	
	Pb ²⁺ /Pb	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13	
	Fe ³⁺ /Fe	$Fe^{3+}(aq) + 3e^- \longrightarrow Fe(s)$	- 0.04	
	H [⊕] /H ₂ , Pt	$2H^{\oplus}(aq) + 2e^- \longrightarrow H_2(g)$	0.00	
	Br [©] /AgBr/Ag	$AgBr(s) + e^{-} \longrightarrow Ag(s) + Br^{\Theta}(aq)$	0.10	
	Cu ²⁺ /Cu [⊕] , Pt	$Cu^{2+}(aq) + e^{-} \longrightarrow Cu^{\oplus}(aq)$	0.15	
	Sn^{4+}/Sn^{2+} , Pt	$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2e^{-} \longrightarrow \operatorname{Sn}^{2+}(\operatorname{aq})$	0.15	

				_
3.14	4 Physical Chemistry	$_{2}$ H SO (ag) + H ₂ O(1)	0.17	
		$SO_4^{2-}(aq) + 4H^{\oplus}(aq) + 2e^- \longrightarrow H_2SO_3(aq) + H_2O(1)$	0.22	
	SO ₄ ²⁻ /H ₂ SO ₃	C((aa) + e - 7)B(0)	0.27	
	Cl [©] /AgCl/Ag Cl [©] /Hg ₂ Cl ₂ /Hg(Pt)	$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(s) + 2Cl^{\Theta}(aq)$	0.34	
	Cu^{2+}/Cu	$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$	0.40	
20	O TT	$O_2(g) + 2H_2O(1) + 4e^- \longrightarrow 4 \text{ OH (aq)}$	0.52	S
ase	Cu [⊕] /Cu	$Cu^{\oplus}(aq) + e^{-} \longrightarrow Cu(s)$	0.54	eas
incre	I ₂ /I [©] , Pt	$1/2I_2(s) + e^- \longrightarrow 1^{\bigcirc}(aq)$	0.68	inci
wer	Pt, O_2/H_2O_2	$O_2(g) + 2H^{\oplus}(aq) + 2e^- \longrightarrow H_2O_2(aq)$	0.77	wer
od s	Fe^{3+}/Fe^{2+} , Pt	$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$	0.79	od S
Oxidising power increases	$Hg_2^{2+}/Hg(Pt)$	$1/2\mathrm{Hg}_2^{2+}(\mathrm{aq}) + e^- \longrightarrow \mathrm{Hg}(\mathrm{s})$	0.80	Reducing power increases
)xid	Ag [⊕] /Ag	$Ag^{\oplus}(aq) + e^{-} \longrightarrow Ag(s)$	0.92	Çedı
	Hg^{2+}/Hg_2^{2+}	$2Hg^{2+}(aq) + 2e^{-} \longrightarrow Hg_2^{2+}(aq)$	0.97	1
	NO₃ [©] /NO, Pt	$NO_3^{\odot} + 4H^{\oplus}(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(1)$	1.09	
	Pt, Br ₂ /Br [⊙]	$Br_2(1) + 2e^- \longrightarrow 2Br^{\odot}(aq)$	1.23	
	MnO_2/Mn^{2+}	$\operatorname{MnO}_2(s) + 4\operatorname{H}^{\oplus}(aq) + 2e^- \longrightarrow \operatorname{Mn}^{2+}(aq) + 2\operatorname{H}_2\operatorname{O}(1)$	1.23	
	H [⊕] /O ₂ /Pt	$O_2(g) + 4H^{\oplus}(aq) + 4e^- \longrightarrow H_2O(l)$	1.33	
	$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-}(aq) + 14H^{\oplus} + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(1)$	1.36	
-	Cl₂/Cl [©]	$1/2 \operatorname{Cl}_2(g) + e^- \longrightarrow \operatorname{Cl}^{\ominus}(s)$	1.40	
	Au ³⁺ /Au	$Au^{3+}(aq) + 3e^{-} \longrightarrow Au(s)$	1.51	
	$\mathrm{MnO_4}^{\odot}/\mathrm{Mn^{2+}},\mathrm{H}^{\oplus}/\mathrm{Pt}$	$\operatorname{MnO_4^{\ominus}}(\operatorname{aq}) + 8\operatorname{H}^{\oplus}(\operatorname{aq}) + 5e^- \longrightarrow \operatorname{Mn^{2+}}(\operatorname{aq}) + 4\operatorname{H_2O}(\operatorname{I})$	1.72	
	Ce^{4+}/Ce^{3+} , Pt	$Ce^{4+}(aq) + e^{-} \longrightarrow Ce^{3+}(aq)$	1.78	
	H_2O_2/H_2O	$H_2O_2(l) + 2H^{\oplus}(aq) + 2e^- \longrightarrow 2H_2O(1)$		
	Co^{3+}/Co^{2+} , Pt	$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	1.81	
	O_3/O_2	$O_3(g) + 2H^{\oplus}(aq) + 2e^- \longrightarrow O_2(g) + H_2O(1)$	2.07	
\downarrow	Pt, F_2/F^{\ominus}	$F_2(g) + 2e^- \longrightarrow 2F^{\ominus}(s)$	2.87	

Lower the reduction potential, higher will be the tendency of forming positive ions. This is related to the reactivity of metals. The order of reactivity of metals: Li > K > Ca > Na > Mg > Al.

In this series, oxidizing character increases and reducing character decreases, e.g., the reducing character follows the order: Na > Mg > Zn > Fe > Ni > Cu > Ag.

A negative E^{\odot} means that the redox couple is a stronger reducing agent than the H^{\oplus} | H_2 couple.

A positive E^{\odot} means that the redox couple is a weaker reducing agent than the H^{\oplus} | H_2 couple.

Various electrodes have thus been arranged in the order of their increasing values of standard reduction potentials. This arrangement is called *electrochemical series*. This also includes in itself the *activity series of metals* because the relative activity of metals can be obtained by comparing their oxidation potentials.

The applications of electrochemical series are as follows:

a. To compare the relative oxidizing and reducing powers:

If the standard reduction potential of an electrode is greater than zero, then its reduced form is more stable compared to H₂ gas. In other words, the substance element or ion is more easily reduced and is a stronger oxidizing agent. Similarly, if the standard electrode potential is negative, then H₂ gas is more stable than the reduced form of the species. In other words, the substance (element or ion) is less easily reduced and is a weaker oxidizing agent.

Thus, it can be seen from the Table 3.1 that standard reduction potential for F_2 is the highest and Li^{\oplus} ions have the lowest reduction potential, which means that F_2 is reduced

to F[⊙] ions most easily whereas Li[⊕] ions is reduced with greatest difficulty.

Therefore, F_2 gas is the strongest oxidizing agent and $F^{\mathbb{Q}}$ ion is the weakest reducing agent. Likewise, Li^{\oplus} ion is the weakest oxidizing agent while Li metal is the most powerful reducing agent in an aqueous solution.

Conversely, writing the reaction in reverse order, it can be seen that Li metal will be oxidized most easily and hence is the best reducing agent whereas F[⊙] ion is oxidized with greatest difficulty and hence is the weakest reducing agent.

b. To compare the relative activities of metals: It can be seen that as we go from top to bottom in Table 3.1, the standard reduction potential increases and with this increases the oxidizing power of the species on the left and decreases the reducing power of the species on the right hand side of the reaction.

Greater the oxidation potential (or lesser reduction potential) of a metal, more easily it can lose electrons and hence greater

is its reactivity. As a result, a metal with greater oxidation is its least oxidation potentials and displace metals with lower oxidation potentials from their salt solution. For example, the oxidation potentials of Mg, Zn, Fe, Cu, and Ag are in the order

$$\frac{\text{of Mg, Zn, Fe}}{\text{Mg}} > \text{Zn} > \text{Fe} > \text{Cu} > \text{Ag.}$$

Hence, each metal can displace metals on its right from the salt solutions. So their reactivity is in the order given above.

Electrochemical cells are used in the determination of pH of the solution, solubility product, equilibrium constant, other thermodynamic properties, and for potentiometric titration.

3.6.1 ELECTROPOSITIVE CHARACTER

The useful mnemonic of remembering the metalic character

Decreasing order of metallic character is given below:

Decreasing order
$$a > b$$

 $K > Na > Ba > Ca > Mg > Al > Zn > Fe > Ni > Sn > Pb$

$$\frac{K}{H} > Cu > Hg > Ag > Au > Pt$$

The useful mnemonic to remember the metallic series is:

$$\begin{bmatrix} P \in B \in C \\ P \in Potassium (K) \\ S \in Sodium (Na) \\ B \in Barium (Ba) \\ C \in Calcium (Ca) \end{bmatrix} \begin{bmatrix} M = Magnesium (Mg) \\ A = Aluminium (Al) \\ Z \in Zinc (Zn) \\ I = Iron (Fe) \\ N = Nickel (Ni) \\ T = Tin (Sn) \\ L = Lead (Pb) \end{bmatrix} \begin{bmatrix} C = Copper (Cu) \\ H = Mercury (Hg) \\ A = Silver (Ag) \\ A = Gold (Au) \\ P = Platinum (Pt) \end{bmatrix}$$

Note: That hydrogen is not a metal and comes between MAZINTL and CHAAP

ILLUSTRATION 3.1

Consider the following cell reaction

$$Zn + 2Ag^{\oplus} \longrightarrow Zn^{2+} + 2Ag.$$

Given that

$$E^{\odot}_{\text{Zn}^{2+}(\text{aq}) \mid \text{Zn (s)}} = -0.76 \text{ V}$$

 $E^{\odot}_{\text{Ag} \oplus (\text{aq}) \mid \text{Ag (s)}} = 0.80 \text{ V}$

- a. Calculate the standard EMF of the cell.
- b. Which ion is more powerful oxidizing agent?
- c. Which metal is more powerful reducing agent?

Sol.

a. The cell reaction is written in two half reactions as:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$
 (oxidation half reaction)

$$2Ag^{\oplus}$$
 (aq) $+2e^{-}$ \longrightarrow $2Ag$ (reduction half reaction)
Here E^{\ominus} is given in standard reduction potential.

Here
$$E^{\odot}$$
 is given in standard reduction pote $E^{\odot}_{Ag} \oplus_{|Ag|} > E^{\odot}_{Zn^{2+}|Zn|}$.

Therefore,
$$Ag^{\oplus} | Ag$$
 will undergo reduction and will act as cathode and $Zn | Zn^{2+}$ will undergo oxidation and will act as anode.

$$\therefore E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$$
$$= 0.80 - (-0.76) = 1.56 \text{ V}$$

Alternatively

Since standard reduction potential of $Ag^{\oplus}\,|\,Ag$ is greater than standard reduction potential of $Zn^{2+}\,|\,Zn,$ thus, $Zn\,|\,$ Zn²⁺ will undergo oxidation and Ag[⊕] | Ag will undergo reduction.

$$E^{\odot}_{\text{oxidation } Zn \mid Zn^{2+}} = -E^{\odot}_{\text{reduction } (Zn^{2+} \mid Zn)}$$

= $-(-0.76) = 0.76 \text{ V}$

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{oxidation}} + E^{\odot}_{\text{reduction}}$$
$$= 0.76 + 0.80 = 1.56 \text{ V}$$

b. Cell reaction:

$$2Ag^{\oplus}(1 M) + Zn(s) \longrightarrow Zn^{2+}(1 M) + 2Ag(s)$$

According to the cell reaction, Ag[⊕] ion is reduced to Ag and hence Ag^{\oplus} ion is a stronger oxidizing agent.

c. According to the cell reaction, Zn(s) is oxidized to Zn²⁺ ions and hence Zn metal is a stronger reducing agent.

ILLUSTRATION 3.2

Can a solution of CuSO₄ be stored in (a) zinc (Zn) pot; (b) silver (Ag) pot?

Sol.

a. From Table 3.1, the standard reduction potential of Zn²⁺|Zn is -0.76 V and standard oxidation potential will be 0.76 V, whereas the standard reduction potential of Cu²⁺ | Cu is 0.34 V and standard oxidation potential will be - 0.34 V.

Therefore, $E_{\text{oxidation }(\text{Zn} \mid \text{Zn}^{2+})}^{\ominus} > E_{\text{oxidation }(\text{Cu} \mid \text{Cu}^{2+})}^{\ominus}$. Hence, Zn is more reactive than Cu. Hence, it displaces Cu from CuSO₄ solution as follows:

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Thus, Zn reacts with CuSO₄ solution. Hence, CuSO₄ solution cannot be stored in Zn pot.

Alternatively

Find E^{\odot}_{cell} . If it is positive, it means cell reaction will occur, and one cannot store the solution in the pot. If the standard oxidation potential of the metal behaving as pot is greater than the standard oxidation potential of the metal consisting of solution, then $E_{\text{cell}}^{\ominus}$ will be positive and one cannot store the solution in the pot.

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$$

$$= E^{\odot}_{\text{Cu}^{2+} \mid \text{Cu}} - E^{\odot}_{\text{Zn}^{2+} \mid \text{Zn}}$$

$$= 0.34 - (-0.76) = 1.10 \text{ V}$$

Therefore, a solution of CuSO₄ cannot be stored in Zn pot.

b. From Table 3.1, the standard reduction potential of Ag^{\oplus} Ag is 0.80 V and standard reduction potential of Cu²⁺ | Cu is 0.34 V.

$$E^{\odot}_{Ag} \oplus_{Ag} > E^{\odot}_{Cu^{2+}|Cu}$$

$$E^{\Theta}_{Ag \mid Ag} \oplus < E^{\Theta}_{Cu \mid Cu^{2+}}$$

Since the standard oxidation potential of the metal (Ag) behaving as pot is less than the standard oxidation potential of the metal consisting of solution (CuSO₄), then E^{\odot}_{cell} will be negative, and one can store the solution (CuSO₄) in the pot of Ag.

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$$

$$= E^{\odot}_{\text{Cu}}^{2+}|_{\text{Cu}} - E^{\odot}_{\text{Ag}}^{\oplus}|_{\text{Ag}}$$

$$= 0.34 - 0.80 = -0.46 \text{ V}$$

Therefore, one can store CuSO₄ in Ag pot.

ILLUSTRATION 3.3

Construct a cell using given electrodes at 298 K and also calculate its standard EMF.

Given:
$$E^{\odot}_{Zn \mid Zn^{2+} = 0.76 \text{ V}}$$

 $E^{\odot}_{Cu^{2+} \mid Cu} = 0.34 \text{ V}$

Sol. Note that $E^{\odot}_{Z_n \mid Z_n^{2+}}$ is the standard oxidation potential value while that of $E^{\odot}_{Cu^{2+}\mid Cu}$ is standard reduction potential value.

Therefore, $E^{\odot}_{\rm Zn^{2+} \mid Zn}$ (standard reduction potential) value is -0.76 V. Comparing the two standard reduction potential values.

$$: E^{\odot}_{(Cu^{2+}|Cu)} > E^{\odot}_{(Zn^{2+}|Zn)}$$

Hence, copper electrode will act as cathode and Zinc electrode will act as anode. The cell representation of the cell is:

$$Zn(s) | Zn^{2+} (1.0 \text{ M}) || Cu^{2+} (1.0 \text{ M}) | Cu(s)$$

 $E^{\odot}_{cell} = (E^{\odot}_{reduction})_{cathode} - (E^{\odot}_{reduction})_{anode}$
 $= 0.34 - (-0.76) = 1.1 \text{ V}$

ILLUSTRATION 3.4

If $E^{\ominus}_{(Ag \mid Ag^{\oplus})} = -0.8 \text{ V}$ and $E^{\ominus}_{(H_2 \mid 2H^{\oplus})} = 0 \text{ V}$, in a cell arrangement using these two electrodes, find $E^{\ominus}_{\text{cell}}$ and find out which electrode acts as anode and which acts as cathode.

Note that $E^{\odot}_{(Ag|Ag^{\oplus})}$ and $E^{\odot}_{H_2|2H^{\oplus}}$ are standard oxidation potential values. Comparing the two values,

$$E^{\ominus}_{(H_2 \mid 2H^{\oplus})} > E^{\ominus}_{(Ag \mid Ag^{\oplus})}$$
 or

Comparing the reduction potential values,

$$E^{\ominus}_{(Ag^{\bigoplus}|Ag)} \geq E^{\ominus}_{(2H^{\bigoplus}|H_2)}$$

Hence, silver electrode will act as cathode and hydrogen electrode will act as anode.

The cell representation of the cell is:

Pt, H₂ (1 atm) | H[⊕] (1.0 M) || Ag[⊕] (1.0 M) |Ag (s)

$$E^{\ominus}_{\text{cell}} = (E^{\ominus}_{\text{reduction}})_{\text{cathode}} - (E^{\ominus}_{\text{reduction}})_{\text{anode}}$$

= 0.8 - 0 = 0.8 V

ILLUSTRATION 3.5

Calculate E^{\odot} for each cell and write the equation for each cell process. Explain the significance of any negative E^{\odot} value.

a.
$$Cd(s) \mid Cd^{2+}(1.0 \text{ M}) \parallel AgNO_3 (1.0 \text{ M}) \mid Ag(s)$$

b. Fe(s) | Fe SO₄ (1.0 M) || ZnSO₄ (1.0 M) | Zn(s)
c. Pt, Cl₂(g) (1 atm) | NaCl (1.0 M) | Hg₂Cl₂(s) | Hg(s)
Given:
$$E^{\odot}_{(Cd)} = -0.40 \text{ V}, \quad E^{\odot}_{(Fe)} = -0.41 \text{ V}, \quad E^{\odot}_{(Zn)} = -0.76 \text{ V}$$

 $E^{\odot}_{(Ag)} = +0.80 \text{ V}, \quad E^{\odot}_{(2Cl^{\odot}|Cl_2)} = -1.36 \text{ V}.$
 $E^{\odot}_{(Hg|Hg_2|Cl_2)} = -0.27 \text{ V}.$

Sol.

a. Anode: $Cd(s) \longrightarrow Cd^{2+} (1.0 M) + 26$ Cathode:

$$2Ag^{\oplus}(1.0 \text{ M}) + 2e \longrightarrow 2Ag(s)$$

Cell reaction:

$$Cd(s) + 2Ag^{\oplus}(1.0 M) \longrightarrow Cd^{2+}(1.0 M) + 2Ag(s)$$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$$

= 0.8 - (- 0.4) = 1.2 V

EMF of cell is positive, hence the cell will function with Cd as anode and Ag as cathode.

b. Anode: Fe (s) \longrightarrow Fe²⁺ (1.0 M) + 2eCathode: Zn²⁺(1.0 M) + 2eCell reaction:

$$Fe(s) + Zn^{2+} (1.0 \text{ M}) \longrightarrow Fe^{2+} (1.0 \text{ M}) + Zn(s)$$

$$E^{\odot} = (E^{\odot} + S) + (E^{\odot} + S)$$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$$

= -0.76 - (-0.41) = -0.35 V.

Negative EMF value suggests that cell will not function in the manner it is represented, i.e., Fe as anode and In as cathode. So reversing (interchanging) the cathode and anode, i.e., making Zn as anode and Fe as cathode can make the cell functional.

c. Anode: $2C1^{\circ}$ (1.0 M) \longrightarrow Cl_2 (1.0 atm) + $2c^{\circ}$ Cathode:

$$Hg_2 Cl_2(s) + 2e \longrightarrow 2Hg(s) + 2Cl^{\circ} (1.0 M)$$

Cell reaction:

$$Hg_2Cl_2(s) \longrightarrow 2Hg(s) + Cl_2(1.0 \text{ am})$$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$$

= 0.27 - (1.36) = -1.09 V

Negative EMF value suggests that the cell will not function in the manner it is represented, i.e., H_2Cl_2 as cathode and $2Cl^{\odot} \mid Cl_2$ as anode. So reversing (interchanging) the cathode and anode, i.e., making H_2Cl_2 (i.e., $Hg \mid Hg_2Cl_2$) as anode and $Cl_2 \mid 2Cl^{\odot}$ as cathode, can make the cell functional.

ILLUSTRATION 3.6

For the reduction of NO_3^{\odot} ion in an aqueous solution, E^{\odot} is 0.96 V. E^{\odot} for some metal ions are given as:

i.
$$Fe^{3+}(aq) + 3e^{-} \longrightarrow Fe(s)$$
, $E^{\odot} = -0.04 \text{ V}$

ii.
$$Hg^{2+}(aq) + 2e^{-} \longrightarrow Hg(s), E^{\odot} = 0.86 \text{ V}$$

iii.
$$V^{2+}(aq) + 2e^{-} \longrightarrow V(s), E^{\odot} = -1.19 \text{ V}$$

iv. $Au^{3+}(aq) + 3e^{-} \longrightarrow Au(s), E^{\odot} = 1.40 \text{ V}$

b. Hg and Fo

a. Fe and Au c. Fe and V

Sol. (b, c, d)

d. V and Hg

$$(b, c, d)$$
 $P = (b, c, d)$
 $P = (b, c, d)$
 $P = (c, d)$

NU₃
Compare the standard reduction potential of the given metals with that of NO₃ eduction.

 $E_{\text{reduction}}^{\odot}$ for NO_3^{\odot} is greater than $E_{\text{reduction}}^{\odot}$ of (i), (ii), and

So, NO₃ will be able to oxidize, Fe, Hg, and V. So correct options are (b), (c), and (d).

ILLUSTRATION 3.7

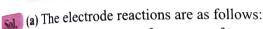
The following electrochemical cell is represented as:

The following
$$p_{(1)}|Hg^{2+}, Hg_2^{2+} (a=1) || Ce^{4+}, Ce^{3+} (a=1) || Pt (2)$$

3. If an ammeter is connected between two platinum electrodes, predict the direction of flow of current.

b. Will the current decrease or increase with time?

Given:
$$E^{\odot}_{2Hg^{2+}|Hg_2^{2+}} = 0.92 \text{ V}; E^{\odot}_{Ce^{4+}/Ce^{3+}} = 1.61 \text{ V}$$



 $Hg_2^{2+} \longrightarrow 2Hg^{2+} + 2e^{-}$ (oxidation) Anode reaction: Cathode reaction:

$$2Ce^{4+} + 2e \longrightarrow 2Ce^{3+}$$
 (Reduction)

Cell reaction: Hg_{2}^{2+} , $2Ce^{4+}$ $\longrightarrow 2Hg^{2+} + 2Ce^{3+}$

$$E_{\text{cell}}^{\odot} = (E_{\text{reduction}}^{\odot})_{c} - (E_{\text{reduction}}^{\odot})_{a}$$
$$= 1.61 \text{ V} - 0.92 \text{ V} = 0.69 \text{ V}$$

Since E^{\odot} cell is positive, the cell reaction is feasible or spontaneous.

Current in electrochemical cell flows from cathode to anode whereas the electrons flow from anode to cathode.

So the current in the circuit will flow from Pt(2) (cathode) to Pt (1) (anode).

b. With the passage of time, EMF of the cell will decrease and so the current will also decrease in the circuit.

ILLUSTRATION 3.8

The following reaction: occurs in the dry cell, called flash light battery, which is used to power radios, clocks, and flashlights:

$$^{2M_{1}O_{2}(s)} + 8 \stackrel{\oplus}{NH_{4}} + Zn(s) \longrightarrow 2Mn^{3+} + 8NH_{3} + Zn^{2+} + 4H_{2}O_{2}(s)$$

a. Write the anode and cathode reactions.

b. Calculate E^{\odot}_{cell} of the dry cell if the electrode potential of cathode ($E^{\odot}_{\text{reduction}}$) varies between 0.49 V and 0.74 V and that of anode $E^{\odot}_{\text{reduction}}$ is -0.76 V.

Sol. The electrode reactions are as follows: Anode reaction:

 $Zn(s) \longrightarrow Zn^{2+} (1.0 \text{ M}) + 2e^{-} \text{ (oxidation)}$ $E^{\odot}_{\text{reduction}} = -0.76 \text{ V}$ Cathode reaction:

Cathode reaction:

$$8 \stackrel{\oplus}{NH_4}(aq) + 2MnO_2(s) + 2e \longrightarrow$$

 $2Mn^{3+}(aq) + 8NH_3(g) + 4H_2O(l)$ (Reduction)

Cell reaction:

$$Zn(s) + 8 \overset{\oplus}{NH_4}(aq) + 2MnO_2 \longrightarrow 2Mn^{3+}(aq) + 8NH_3(g) + Zn^{2+} + 4H_2O(l)$$

 $(E_{\text{reduction}}^{\odot})_{\text{cathode}}$ varies between 0.49 to 0.74 V.

For
$$(E^{\odot}_{\text{reduction}})_{\text{cathode}} = 0.49 \text{ V}$$
,
 $E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{cathode}} - (E^{\odot}_{\text{reduction}})_{\text{anode}}$
 $= 0.49 - (-0.76) = 1.25 \text{ V}$

For
$$(E^{\odot}_{\text{reduction}})_{\text{cathode}} = 0.74 \text{ V},$$

$$E^{\Theta}_{\text{cell}} = 0.74 - (-0.76) = 1.50 \text{ V}$$

 E^{\odot}_{cell} varies between 1.25 V and 1.50 V.

3.7 NERNST EQUATION

In electrochemistry, the Nernst equation is an equation that can be used (in conjunction with other information) to determine the equilibrium reduction potential of a half cell in an electrochemical cell. It can also be used to determine the total voltage (EMF) for a full electrochemical cell. It is named after the German physical chemistry who first formulated it, Walther Nernst.

3.7.1 EFFECT OF CONCENTRATION ON EMF OF CELLS AND HALF CELLS (FOR AN ELECTRODE $M^{n+} | M$

In the calculation of standard EMF of the half cell and standard EMF of a cell, we have assumed that the concentration of all species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for an electrode reaction:

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

The electrode potential at any concentration measured with respect to hydrogen electrode can be represented by:

$$E_{(M^{n+}|M)} = E_{(M^{n+}|M)}^{\ominus} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

But concentration of solid M is taken as unity, we have

$$E_{(M^{n^{+}}|M)} = E^{\odot}_{(M^{n^{+}}|M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n^{+}}]}$$

$$= E^{\odot}_{(M^{n^{+}}/M)} - \frac{2.303}{nF} \log \frac{1}{[M^{n^{+}}]} \qquad \dots (i)$$

where $E^{\odot}_{(\mathbf{M}^{n^+} \mid \mathbf{M})}$ has already been defined R is the gas constant (8.314 J K⁻¹ mol⁻¹). F is the Faraday constant or charge on 1 mol electrons = 96487 coulomb mol⁻¹ ≈ 96500 C mol⁻¹. Temperature is in kelvin and $[M^{+n}]$ is the concentration of the species M^{n+} , n is the number of electron(s) transferred in the balanced cell reaction.

Substituting the values at 298 K in Eq. (i), we get,

Substituting the varieties
$$E_{(M^{n+}|M)} = E^{\odot}_{(M^{n+}|M)}$$

$$-\frac{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{n \times 96487 \text{ C mol}^{-1}} \log \frac{1}{[M^{n+}]}$$

=
$$E^{\odot}_{(M^{n+}|M)} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$
 (at 298 K) ...(ii)

Note: The values of $\left(\frac{2.303RT}{F}\right)$ at various temperatures are as follows:

Temperature	Values of $\left(\frac{2.303RT}{F}\right)$
273 K (0°C)	0.054
278 K (5°C)	0.055
283 K (10°C)	0.056
288 K (15°C)	0.057
293 K (20°C)	0.058
298 K (25°C)	0.059
303 K (30°C)	0.060
308 K (35°C)	0.061

3.7.2 EMF OF THE CELL FOR A GENERAL **ELECTROCHEMICAL REACTION**

The Nernst equation for determining the EMF of the cell for a general electrochemical reaction of the type

$$aA + bB \xrightarrow{ne^-} cC + dD$$

can be written as

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{n_{\text{cell}}} \log Q_{\text{cell}}$$
$$= E^{\odot}_{\text{cell}} - \frac{0.059}{n_{\text{cell}}} \log \frac{[C]^{c}[D]^{d}}{[A]^{a} [B]^{b}}$$

where Q_{cell} is the reaction coefficient of overall reaction, $E_{\mathrm{cell}}^{\odot}$ is the standard EMF of the cell, and n_{cell} is the number of electrons transfer in the cell reaction. For example, in Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions at 298 K, we have

For cathode:

$$E_{(Cu^{2+}|Cu)} = E^{\odot}_{(Cu^{2+}/Cu)} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}(aq)]}$$

$$E_{(Z_n^{2^+}|Z_n)} = E^{\odot}_{(Z_n^{2^+}/Z_n)} - \frac{0.059}{2} \log \frac{1}{[Z_n^{2^+}(aq)]}$$

The cell potential,

$$E_{\text{cell}} = E_{(Cu^{2+} \mid Cu)} - E_{(Zn^{2+} \mid Zn)}$$

$$= E^{\bigcirc}_{(Cu^{2+} \mid Cu)} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+} (aq)]}$$

$$- E^{\bigcirc}_{(Zn^{2+} \mid Zn)} + \frac{0.059}{2} \log \frac{1}{[Zn^{2+} (aq)]}$$

$$= E^{\bigcirc}_{(Cu^{2+} \mid Cu)} - E^{\bigcirc}_{(Zn^{2+} \mid Zn)}$$

$$- \frac{0.059}{2} \left[\log \frac{[Zn^{2+}]}{[Cu^{2+}]} \right]$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$
 ...(ii)

From Eq. (iii), it is evident that $E_{\text{cell depends } 0\eta}$ for Cu^{2+} and Zn^{2+} ions. It increases with $\ln z$ From Eq. (iii), it is evident concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increases with $\frac{1}{\log r_{c_1}}$ with $\frac{1}{\log r_{c_2}}$ with $\frac{1}{\log r_{c_3}}$ wit

Note: Use the same number of electrons (n) for both the

3.7.3 EMF OF HYDROGEN ELECTRODE IN DIFFEREN

For half electrode, write the equation of reduction and use standard hydrogen electrons. For half electrode, which reduction potential value. For example, hydrogen electrode dipped

$$2H^{\oplus} + 2e^{-} \longrightarrow H_{2}(g) (1 \text{ atm})$$

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.059}{2} \log \frac{p_{\text{H}_{2}}}{[\text{H}^{\oplus}]^{2}}$$

$$= 0 - \frac{0.059}{2} \log \frac{1 \text{ atm}}{[\text{H}^{\oplus}]^{2}}$$

$$= -\frac{0.059}{2} \log [\text{H}^{\oplus}]^{-2}$$

$$= -0.059 \log [-\log [\text{H}^{\oplus}]]$$

$$= -0.059 \text{ pH}.$$

$$\therefore E_{2H^{\oplus}|_{\text{H}_{2}}} = -0.059 \text{ pH}$$

3.7.4 EQUILIBRIUM CONSTANT FROM NERNST EQUATION $(E_{CELL} = 0.0 \text{ V})$

If the circuit in Daniell cell is closed, the following reaction takes place:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

With time, $[Zn^{2+}]$ increases while $[Cu^{2+}]$ decreases and at the same time voltage of the cell on the voltmeter decreases. After some time there happens to be no change in the [Cu2+] and [Zn2+] ions, and at the some time, voltmeter gives zero reading This indicates that equilibrium is attained, and the Nernst equation becomes

$$E_{\text{cell}} = 0 = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$
or $E_{\text{cell}}^{\odot} = \frac{0.059 \text{ V}}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$
But at equilibrium,
$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_{\text{e}} \text{ at } 298 \text{ K}$$

Evaluate equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c \text{ at } 298 \text{ K}$$

$$\therefore E^{\odot}_{\text{cell}} = \frac{0.059 \text{ V}}{2} \log K_c$$

$$1.1 \text{ V} = \frac{0.059 \text{ V}}{2} \log K_c$$

$$\therefore \log K_c = \frac{(1.1 \text{ V} \times 2)}{0.059 \text{ V}} = 37.288$$

$$K_{\rm c} = 2 \times 10^{37} \text{ at } 298 \text{ K}$$

$$\int_{0}^{\infty} \frac{0.059}{100} \log K_{c} \qquad \dots (i)$$

Eq. (i) gives a relationship between equilibrium constant must be colling and standard potential of the colling area. has reaction and standard potential of the cell in which that the reaction takes place. Thus, equilibrium constants of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, additicult to measure otherwise. can be seen to difficult to measure otherwise. partion land F reaction, is difficult to measure otherwise, can be calculated from which is appending E^{\odot} value of the cell. when is a conference of the cell. We confess ponding E^{\odot} value of the cell.

3.8 ELECTROCHEMICAL CELL AND GIBBS ENERGY OF THE REACTION

work done in one second is equal to the electrical poential multiplied by total charge passed. To calculate maximum mork from a galvanic cell, the charge has to be passed reversibly. The maximum work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the EMF of the cell is E and is the amount of charge passed, then work done by the cell and $_{\text{libbs}}$ energy of the reaction (Δ, G) is:

Work done by the cell = Charge \times Potential

Work done by the cell is equal to the decrease in the free energy.

$$-\Delta_{r}G = nFE_{\text{cell}}$$

Note: E_{cell} is an intensive property but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n.

Similarly, maximum obtainable work from a cell at standard condition will be:

$$W_{\text{max}} = nFE^{\odot}_{\text{cell}}$$

$$-\Delta_{r}G^{\odot} = nFE^{\odot}_{cell}$$

Thus, for the reaction:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$$\Delta_{\rm r}G = -2 FE_{\rm cell}$$

But for the reaction.

$$2Zn(s) + 2Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$$\Delta_{\rm r}G = -4 \ FE_{\rm cell}$$

If the concentration of all the reacting species is unity, then $E_{\text{cell}} = E_{\text{cell}}^{\Theta}$ and we have

$$\Delta_{r}G^{\Theta} = -nFE^{\Theta}_{cell}$$

Thus, from the measurement of E^{\odot}_{cell} , $\Delta_{\text{r}}G^{\odot}$ (standard free energy) of the reaction, an important thermodynamic property can be

From $\Delta_{\rm r} G^{\odot}$, equilibrium constant of the reaction can be

$$\Delta_{\rm r}G^{\odot} = -RT \ln K$$

(or)
$$\Delta_{\rm r} G^{\odot} = -2.303RT \log K$$

$^{3.8.1}$ Variation of EMF ($E_{\rm cell}$) with Temperature

a. Using Gibbs Helmholtz equation, the temperature coefficient of the EMF of the cell is written as

$$\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT} \right]_P$$
 (at constant pressure) ...(i)

(since
$$\Delta G = -nFE_{\text{cell}}$$
)
 $\Rightarrow -nF E_{\text{cell}} = \Delta H + T \left[\frac{d(-nFE_{\text{cell}})}{dT} \right]_P$
 $= \Delta H - nFT \left(\frac{dE_{\text{cell}}}{dT} \right)_P$
 $\Rightarrow \left(\frac{dE_{\text{cell}}}{dT} \right)_P = \frac{\Delta H}{nFT} + \frac{E_{\text{cell}}}{T}$...(ii)

b. Enthalpy change from Eq. (i):

$$\Delta H = -nFE_{\text{cell}} + nFT \left(\frac{dE_{\text{cell}}}{dT}\right)_{P}$$
$$= -nF \left[E_{\text{cell}} - T \left(\frac{dE_{\text{cell}}}{dT}\right)_{P}\right]$$

c. Enthalpy change can be determined by comparing Eq. (i) with $\Delta G = \Delta H - T \Delta S$.

$$\Delta S = -\left(\frac{d(\Delta G)}{dT}\right)_{P}$$

$$= -\left[\frac{d}{dT}(-nFE_{\text{cell}})_{P}\right]$$

$$= nF\left(\frac{dE_{\text{cell}}}{dT}\right)_{P}$$

ILLUSTRATION 3.9

Represent the cell in which following reaction takes place:

 $Mg(s) + 2Ag^{\oplus}(0.0001 \text{ M}) \rightarrow Mg^{2+}(0.130 \text{ M}) + 2Ag(s)$ calculate its E_{cell} if $E_{\text{cell}}^{\ominus} = 3.17 \text{ V}$.

Sol. The cell is represented as:

 $Mg \mid Mg^{2+} (0.130 \text{ M}) \parallel Ag^{\oplus} (0.0001 \text{ M}) \mid Ag$

Reaction at anode:

$$Mg(s) \longrightarrow Mg^{2+} (0.130 M) + 2e^{-}$$

Reaction at cathode:

$$2Ag^{\oplus}(0.0001 \text{ M}) + 2e^{-} \longrightarrow 2Ag(s)$$

Cell reaction:

$$Mg(s) + 2 Ag^{\oplus}(0.0001 M) \longrightarrow Mg^{2+}(0.130 M) + 2Ag(s)$$

$$\therefore E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Mg}^{2^{+}}]}{[\text{Ag}^{\oplus}]^{2}}$$

$$= 3.17 \text{ V} - \frac{0.059}{2} \log \frac{0.130}{(0.0001)^{2}}$$

$$= 3.17 \text{ V} - 0.21 \text{ V} = 2.96 \text{ V}$$

ILLUSTRATION 3.10

Calculate the reduction potential of the following electrodes:

- a. Pt, H₂ (4 atm) | H₂ SO₄ (0.01 M)
- **b.** Pt, H_2 (1 atm) | HCl (0.2 M)
- c. Calculate the potential of hydrogen electrode in contact with a solution whose

i.
$$pH = 5$$
 ii. $pOH = 4$

Sol.

('n' factor for $H_2SO_4 = 2$) a. Half cell reaction:

 H_2 (4 atm) $\longrightarrow 2H^{\oplus}$ (0.01 M or 0.02 N) + $2e^{-}$

$$E_{(H_2|2H^{\oplus})} = E^{\ominus}_{(H_2|2H^{\oplus})} - \frac{0.059}{2} \log \frac{[H^{\oplus}]^2}{p_{H_2}}$$

$$= 0 - \frac{0.059}{2} \log \frac{(0.02)^2}{4 \text{ atm}}$$

$$= -\frac{0.059}{2} \log \left(\frac{0.02 \times 0.02}{4}\right)$$

$$= -\frac{0.059}{2} \log (10^{-4})$$

$$= -\frac{0.059}{2} \times -4 \log 10$$

$$= 0.059 \times 2 = 0.118 \text{ V}$$

$$E_{(2H^{\oplus}|H_2)} = -0.118 \text{ V}$$

Note: The concentration of gases is taken as the partial pressure of gases in atmospheric units (atm).

b. Half cell reaction: ('n' factor for HCl = 1)

$$H_2$$
 (1 atm) $\longrightarrow 2H^{\oplus}$ (0.2 M or 0.2 N) + 2 e^{-}

$$E_{(H_2|2H^{\oplus})} = E^{\ominus}_{(H_2/2H^{\oplus})} - \frac{0.059}{2} \log \frac{[H^{\oplus}]^2}{[p_{H_2}]}$$

$$= 0 - \frac{0.059}{2} \log \frac{(0.2 \times 0.2)}{1 \text{ atm}}$$

$$= -\frac{0.059}{2} [\log (4 \times 10^{-2})]$$

$$= -\frac{0.059}{2} [2 \log 2 - 2]$$

$$= -\frac{0.059}{2} (2 \times 0.3 - 2) \quad (\log 2 \approx 0.3)$$

$$= -\frac{0.059}{2} \times -1.4 = 0.059 \times 0.7 = 0.0413 \text{ V}$$

$$E_{(2H^{\oplus} \mid H_2)} = -0.0413 \text{ V}$$

c. i. Use direct formula for the potential (EMF) of hydrogen electrode.

$$E_{(2H^{\bigoplus} \mid H_2)} = -0.059 \text{ pH} = -0.059 \times 5 \text{ V}$$

= -0.295 V

ii. pOH = 4,
$$\therefore$$
 pH = 14 - 4 = 10
 $E_{(2H^{\oplus}|H_2)} = -0.059 \text{ pH} = -0.059 \times 10 \text{ V}$
= -0.59 V

ILLUSTRATION 3.11

For the cell:

 $Zn(s) | Zn^{2+}(a M) || Ag^{\oplus}(b M) | Ag(s).$

- a. Write Nernst equation to show how $E_{\rm cell}$ vary with concentration of Zn^{2+} and Ag^{\oplus} ions. Given $E^{\ominus}_{(Zn^{2+} \mid Zn)}$ = $-0.76 \text{ V}, E^{\odot}_{(Ag^{\bigoplus}|Ag)} = 0.80 \text{ V}.$
- **b.** Find E_{cell} for $[Zn^{2+}]=0.01$ M and $[Ag^{\odot}]=0.02$ M.
- c. For what values of Q will the cell EMF be

i. 0.0 V

ii. 0.97 V

Sol.

a. Anode reaction:

$$Zn(s) \longrightarrow Zn^{2+} (a_{M)+} \chi$$

Cathode reaction:

$$2 \operatorname{Ag}^{\oplus} (b \operatorname{M}) + 2e \longrightarrow 2 \operatorname{Ag}(s)$$

Cell reaction: $Zn(s) + 2 Ag^{\oplus} (b M) \longrightarrow$

$$Zn^{2+} (a M) + 2 Ag(s)$$

$$E^{\odot}_{cell} = (E^{\odot}_{reduction})_{c} - (E^{\odot}_{reduction})_{a}$$

$$= 0.80 - (-0.76) = 1.56 \text{ y}$$

Using Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{n_{\text{cell}}} \log \frac{[Zn^{2+}]}{[Ag^{\oplus}]^2}$$

(Activity of Zn(s) and Ag(s) = 1)

$$= E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log [\text{Zn}^{2+}] + \frac{0.059}{2} \log [\text{Ag}^{\oplus}]^{2}$$

 $(\log 5 \approx 0.7)$

Therefore, E_{cell} will decrease when $[Zn^{2+}]$ increases and [Ag[⊕]] decreases.

b. If $[Zn^{2+}] = 0.01 \text{ M}$ and $[Ag^{\oplus}] = 0.02 \text{ M}$

$$E_{\text{cell}} = 1.56 \text{ V} - \frac{0.059}{2} \log \frac{0.01}{(0.02)^2}$$

$$= 1.56 \text{ V} - \frac{0.059}{2} [\log 25]$$

$$= 1.56 \text{ V} - \frac{0.059}{2} [2 \log 5]$$

$$= 1.56 \text{ V} - \frac{0.059}{2} \times 2 \times 0.7$$

$$= 1.56 \text{ V} - 0.059 \times 0.7$$

c. i.
$$E_{\text{cell}} = 0.0 \text{ V}$$
, $E_{\text{cell}}^{\odot} = 1.56 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log Q_{\text{cell}}$$

=1.56 - 0.0413 = 1.5187 V

$$0.0 = 1.56 - \frac{0.059}{2} \log Q_{\text{cell}}$$

$$\log Q_{\text{cell}} = \frac{2 \times 1.56}{0.059} = 52.88$$

$$Q_{\text{cell}} = \text{Antilog} (52.88) = 7.586 \times 10^{52}$$

ii.
$$E_{\text{cell}} = 0.97 \text{ V}, E_{\text{cell}}^{\odot} = 1.56 \text{ V}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log Q_{\text{cell}}$$

$$0.97 = 1.56 - \frac{0.059}{2} \log Q_{\text{cell}}$$

$$\log Q_{\text{cell}} = \frac{2 \times 0.59}{0.059} = 20$$

$$Q_{\text{cell}} = \text{Antilog} (20) = 10^{20}$$

LUSTRATION 3.12 College the potential of the following half-cells | cells:

$$\frac{|C|^{1/Cr^{3+}}(0.1 \text{ M})||Fe^{-1/Cr^{3+}}(0.1 \text{ M})$$

$$\frac{\text{Given: } E^{\circ} \text{Cr}^{3+} | \text{Cr}}{\text{Given: } E^{\circ} \text{Cr}^{3+} | \text{Cr}} = -0.74 \text{ V} \quad E^{-} \text{Fe}^{2+} | \text{Fe} = -0.44 \text{ V}$$

$$\frac{\text{Given: } E^{\circ} \text{Cr}^{3+} | \text{Cr}}{\text{Given: } E^{\circ} \text{Color}} = 0.44 \text{ V}$$

$$\text{Br}^{\circ} \text{Color} = 0.44 \text{ V}$$

$$\text{Br}^{\circ} \text{Color} = 0.44 \text{ V}$$

$$\text{Br}^{\circ} \text{Color} = 0.44 \text{ V}$$

$$\text{Br}^{\circ} = 0.61 \text{ V}$$

$$\lim_{\theta \to BO_3} E^{\Theta}(BrO_3^{\Theta} | Br^{\Theta}) = 0.61 \text{ V},$$

$$\lim_{\theta \to BO_3} E^{\Theta}(BrO_3^{\Theta} | Br^{\Theta}) = 0.61 \text{ V}.$$

Given:
$$E^{\circ}(BrO_3^{\circ}) = 10^{-3} \text{ M}$$
; $[Br^{\odot}] = 5.0 \times 10^{-3} \text{ M}$, $pH = 9.0$

$$[BrO_3^{\odot}] = 2.5 \times 10^{-1} M, [EF]$$
 for $M, pH = 5$.
 $[BrO_3^{\odot}] = 2.5 \times 10^{-1} M, [EF]$ for $M, pH = 5$.
 $[BrO_3^{\odot}] = 2.5 \times 10^{-1} M, [EF]$ for $M, pH = 5$.

$$_{\text{Given: } E_{(Ag^{\oplus} | Ag)}}^{\text{Ag } | Ag} = 0.80 \text{ V}, E_{(Cl_2 | 2Cl)}^{\odot} = 1.36 \text{ V}$$

Given:
$$E_{(Ag^{\oplus}|Ag)}$$
 $E_{(Ag^{\oplus}|Ag)}$ $E_{$

Given:
$$E^{\odot}_{NO_3}^{\odot} \mid_{NO_2} = 0.78 \text{ V}$$

What will be the reduction potential of the half cell in neutral solution? Assuming all the other species to be at unit concentration.



a. Anode reaction:

$$Cr(s) \longrightarrow Cr^{3+} (0.1 \text{ M}) + 3e^{-1}] \times 2$$

Cathode reaction:

$$[2\overline{e} + Fe^{2+} (0.01 \text{ M}) \longrightarrow Fe (s)] \times 3$$

Cell reaction:

$$2Cr(s) + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe(s)$$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{c}} - (E^{\odot}_{\text{reduction}})_{\text{a}}$$

= -0.44 - (-0.74) = 0.3 V

Using Nernst equation: $(n_{\text{cell}} = 6)$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

Note: Take $0.059 \approx 0.06$, and activity of Cr(s) and Fe(s) is unity.

$$= 0.3 \text{ V} - \frac{0.06}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.3 \text{ V} - 0.01 \log \frac{0.1 \times 0.1}{0.01 \times 0.01 \times 0.01}$$

$$= 0.3 \text{ V} - 0.01 [\log 10^4]$$

$$= 0.3 \text{ V} - 0.01 \times 4 = 0.26 \text{ V}$$

b. Using Nernst equation: $(n_{\text{cell}} = 6, \text{ take } 0.059 \approx 0.06)$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.06}{6} \log \frac{[\text{Br}^{\odot}][\text{OH}]^6}{[\text{BrO}_3^{\odot}]}$$

$$(pH = 9.0, pOH = 14 - 9 = 5, [OH] = 10^{-5} M.$$

Activity of
$$H_2O = 1$$
)

$$E_{(\text{BrO}_3^{\odot} | \text{Br}^{\odot})} = E^{\odot}_{(\text{BrO}_3^{\odot} | \text{Br}^{\odot})} - \frac{0.06}{6} \log \frac{5.0 \times 10^{-3} \times (10^{-5} \text{M})^6}{2.5 \times 10^{-3} \text{M}}$$

$$= 0.61 \text{ V} - 0.01 (\log 2 \times 10^{-30})$$

$$= 0.61 \text{ V} - 0.01(0.3 - 30) \quad (\log 2 \approx 0.3)$$

$$= 0.61 \text{ V} - 0.01 \times (-29.7)$$

$$= 0.61 \text{ V} + 0.297 \text{ V} \approx 0.907 \text{ V}$$

c. Anode reaction: $2Ag(s) \longrightarrow 2Ag^{\oplus}(0.1 \text{ M}) + 2e^{-2}$

Cathode reaction:

$$Cl_2(g) (0.5 \text{ atm}) + 2e^{-} \longrightarrow 2Cl^{\odot} (0.02 \text{ M})$$

Cell reaction:

$$\overline{E_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{c}} - (E^{\odot}_{\text{reduction}})_{\text{a}}}$$

$$= 1.36 \text{ V} - 0.80 \text{ V} = 0.56 \text{ V}$$

Using Nernst equation: $(n_{cell} = 2, activity of Ag = 1, take)$ $0.059 \approx 0.06$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.06}{2} \log \frac{[\text{Ag}^{\oplus}]^2 [\text{Cl}^{\ominus}]^2}{(p_{\text{Cl}_2(g)})}$$

$$E_{\text{cell}} = 0.56 \text{ V} - 0.03 \left(\log \frac{(0.1)^2 (0.2)^2}{0.5 \text{ atm}} \right)$$

$$= 0.56 \text{ V} - 0.03 (\log 8 \times 10^{-4})$$

$$= 0.56 \text{ V} - 0.03(\log 2^3 + \log 10^{-4})$$

$$= 0.56 \text{ V} - 0.03(3 \log 2 - 4)$$

$$(\log 2 \approx 0.3)$$

$$= 0.56 \text{ V} - 0.03(3 \times 0.3 - 4)$$

$$= 0.56 \text{ V} + 0.03 \times 3.1 \text{ V}$$

$$= 0.653 \text{ V}$$

d. pH of neutral solution = $7 : [H^{\oplus}] = 10^{-7} \text{ M}$.

$$n_{\text{cell}} = 1$$
, concentration of $[\text{NO}_2] = [\text{H}_2\text{O}] = [\text{NO}_3^{\odot}] = 1$

$$\begin{split} \mathbf{E}_{(\mathrm{NO_3}^{\odot} | \, \mathrm{NO_2})} &= E^{\odot}_{(\mathrm{NO_3}^{\odot} | \, \mathrm{NO_2})} - \frac{0.059}{1} \log \frac{[\mathrm{NO_2}] [\mathrm{H_2O}]}{[\mathrm{NO_3}^{\odot}] [\mathrm{H}^{\oplus}]^2} \\ &= 0.78 \, \mathrm{V} - 0.059 \log \frac{1}{(10^{-7})^2} \\ &= 0.78 \, \mathrm{V} - 0.059 \, [\, \log \, 10^{14}] \\ &= 0.78 \, \mathrm{V} - 0.059 \times 14 \end{split}$$

ILLUSTRATION 3.13

The solution of CuSO₄ in which Cu rod is dipped is diluted to 10 times, the reduction electrode potential will:

- a. Decrease by 0.03 V
- **b.** Decrease by 0.059 V
- c. Increase by 0.03 V
- d. Increase by 0.059 V

Sol. a.

$$Cu^{2+}$$
 (aq) + $2e^- \longrightarrow Cu$ (s)

Using Nernst equation initially.

=-0.046 V

$$E_{(Cu^{2+}/Cu)initial} = E^{\odot}_{(Cu^{2+}|Cu)} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]_{initial}}$$

Using Nernst equation after dilution.

$$\begin{aligned} E_{\text{(Cu}^{2+}|\text{Cu})\text{final}} &= E^{\odot}_{\text{(Cu}^{2+}|\text{Cu})} - \frac{0.059}{2} \log \frac{1}{[\text{Cu}^{2+}]_{\text{final}}} \\ &(E_{\text{Cu}^{2+}|\text{Cu}})_{\text{final}} - (E_{\text{Cu}^{2+}|\text{Cu}})_{\text{initial}} \\ &= \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]_{\text{final}}}{[\text{Cu}^{2+}]_{\text{initial}}} \\ &= \frac{0.059}{2} \log \left(\frac{1}{10}\right) \end{aligned}$$

Reduction potential of the electrode decreases by 0.03 V.

 $=\frac{0.059}{2}\times(-1)=-0.03 \text{ V}$

ILLUSTRATION 3.14

For the cell:

Tl $|Tl^{\oplus} (10^{-3} \text{ M}) \parallel Cu^{2+} (10^{-1} \text{ M}) \mid Cu$

E_{cell} can be increased by

Decreasing [Cu²⁺]

b. Decreasing [Tl[⊕]]

c. Increasing [Cu²⁺]

d. Increasing by [Tl[⊕]]

(b, c)

Anode reaction:

$$2\text{Tl(s)} \longrightarrow 2\text{Tl}^{\oplus}(10^{-3} \text{ M}) + 2e^{-1}$$

Cathode reaction:

$$Cu^{2+}(10^{-1} M) + 2e^{-} \longrightarrow Cu(s)$$

Cell reaction:

$$2\text{Tl}(s) + \text{Cu}^{2+}(10^{-1} \text{ M}) \longrightarrow 2\text{Tl}^{\oplus}(10^{-3} \text{ M}) + \text{Cu}(s)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{[\text{TI}^{\oplus}]^2}{[\text{Cu}^{2+}]}$$

$$= E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log [\text{TI}^{\oplus}]^2 + \frac{0.059}{2} \log [\text{Cu}^{2+}]$$

$$= E_{\text{cell}}^{\ominus} - 0.059 \log [\text{TI}^{\oplus}] + \frac{0.059}{2} \log [\text{Cu}^{2+}]$$

 E_{cell} can be increased by decreasing [Tl $^{\oplus}$] or increasing

ILLUSTRATION 3.15

A zinc electrode is placed in 0.1 M solution of ZnSO₄ at 25°C. Assuming salt is dissociated to the extent of 20% at this dilution. The potential of this electrode at this temperature is:

$$(E_{Z_n^{2+}|Z_n}^{\odot} = -0.76 \text{ V})$$

a. 0.79 V **b.** -0.79 V

c. -0.81 V

d. 0.81 V

Sol. c.
$$[Zn^{2+}] = 0.1 \times \frac{20}{100} = 0.02 \text{ M}$$

Half cell reaction:

$$Zn^{2+}(0.02 \text{ M}) + 2e^- \longrightarrow Zn(s)$$

$$E_{(Zn^{2+}|Zn)} = E^{\circ}_{(Zn^{2+}|Zn)} - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]}$$
$$= -0.76 \text{ V} - \frac{0.059}{2} \log \frac{1}{0.02 \text{ M}}$$

$$= -0.76 \text{ V} - \frac{0.059}{2} (\log 50)$$

$$= -0.76 \text{ V} - \frac{0.059}{2} (\log 5 + \log 10)$$

$$= -0.76 \text{ V} - \frac{0.059}{2} (0.7 + 1) \quad (\log 5 \approx 0.0)$$

$$= -0.76 \text{ V} - \frac{0.059}{2} \times 1.7 \quad (\text{Take } 0.059 \approx 0.0)$$

$$= -0.76 \text{ V} - 0.03 \times 1.7$$

$$= -0.76 \text{ V} - 0.051 \text{ V}$$

$$= -0.811 \text{ V}$$

ILLUSTRATION 3.16

If excess of Zn is added to 1.0 M solution of CuSO₄, find the concentration of Cu2+ ions at equilibrium.

Given:
$$E^{\odot}_{(Zn^{2+}|Zn)} = -0.76 \text{ V}$$

$$E^{\odot}_{(Cu^{2+}|Cu)} = 0.34 \text{ V}$$

Sol. At equilibrium, $E_{\text{cell}} = 0.0 \text{ V}$ and reaction coefficient

$$E_{\text{cell}}^{\ominus} = (E_{\text{reduction}}^{\ominus})_{c} - (E_{\text{reduction}}^{\ominus})_{a}$$
$$= 0.34 - (-0.76) = 1.10 \text{ V}$$

At equilibrium,

$$E^{\odot}_{\text{cell}} = \frac{0.059}{n_{\text{cell}}} \log K_{\text{eq}}$$

$$\therefore \log K_{\text{eq}} = \frac{E^{\odot}_{\text{cell}} \times n_{\text{cell}}}{0.059} = \frac{1.10 \times 2}{0.059}$$

$$= 37.30$$

$$\therefore K_{\text{eq}} = \text{Antilog} (37.30) = 2.02 \times 10^{37}$$

(Antilog of $0.30 \approx 2$)

Let a M is $[Cu^{2+}]$ at equilibrium

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+} + Cu^{2+}$$

Initial conc.

Final conc.

 $[:a^{\approx 1}]$

Note: Zn is in excess, so $[Zn] = \infty$

$$K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{\alpha}{1-\alpha} \approx \frac{1}{1-\alpha}$$

Since the value of equilibrium constant (2.0×10^{37}) is very high and activity of Zn(s) and activity of Cu(s) = 1

$$\Rightarrow \frac{1}{1-\alpha} = K_{\text{eq}}$$

$$\Rightarrow 1 - \alpha = \frac{1}{K_{eq}} = \frac{1}{2.0 \times 10^{37}} = 5 \times 10^{-38} \text{ M}$$

$$\Rightarrow$$
 $[Cu^{2+}]_{eq} = (1 - \alpha) = 5 \times 10^{-38} \text{ M}$

LUSTRATION 3.17 in a solution of NaI is added to 20 Find the reduction 18 mL of 0.1 N solution of NaI is added to 20 mL of 0.1 when 18 mL of 0.1 N solution at pH = 5. The standard roduction when 18 mL of 0.1 added to 20 mL of 0.1 N^{18} , AsO_4 solution at pH = 5. The standard reduction potential N^{18} , AsO_4 solution at pH = 5. The standard reduction potential $N_{01}^{NO3} AsO_{4}^{3-1} AsO_{2}^{\odot} = -0.70 \text{ V}.$

Half cell reaction:

Half cell reaction:

$$H_{4H}^{\oplus} + AsO_4^{3-} + 2e^- \longrightarrow AsO_2^{\ominus} + 2H_2O$$

$$E_{(AsO_4^{3-}|AsO_2^{\ominus})} = E^{\ominus}_{(AsO_4^{3-}|AsO_2^{\ominus})}$$

$$E_{(AsO_4^{3-}|AsO_2^{\odot})} = E^{\odot}_{(AsO_4^{3-}|AsO_2^{\odot})} - \frac{0.059}{2} \log \frac{[AsO_2^{\odot}]}{[AsO_4^{3-}][H^{\oplus}]^4} \qquad \dots (i)$$

mEq of AsO₄³⁻ =
$$20 \times 0.1 = 2$$

mEq of
$$I^{\odot} = 18 \times 0.1 = 1.8$$

Therefore, 1.8 mEq of I[©] reacts with 1.8 mEq of AsO₄³⁻ to give 1.8 mEq of AsO_2^{\odot} .

give 1.6 ind
$$\frac{1}{2}$$

So, mEq of AsO₄³⁻ left = 2 - 1.8 = 0.2 mEq.

Total volume of solution = (18 + 20) mL = 38 mL

Hence,
$$[AsO_4^{3-}] = \frac{0.2 \text{ mEq}}{38 \text{ mL}}, \ [AsO_2^{\odot}] = \frac{1.8 \text{ mEq}}{38 \text{ mL}}$$

$$_{\rm pH} = 5 \Rightarrow [{\rm H}^{\oplus}] = 10^{-5} {\rm M}$$

Substituting the values in Eq. (i),

$$E_{(\text{AsO}_4^{3-}|\text{AsO}_2^{\odot})} = E^{\odot}_{(\text{AsO}_4^{3-}|\text{AsO}_2^{\odot})} - \frac{0.059}{2} \log \frac{[\text{AsO}_2^{\odot}]}{[\text{AsO}_4^{3-}][\text{H}^{\oplus}]^4}$$

$$= -0.70 \text{ V} - \frac{0.059}{2} \log \frac{(1.8/38)}{\left(\frac{0.2}{38}\right) (10^{-5})^4}$$

$$= -0.70 \text{ V} - \frac{0.059}{2} \log \left(\frac{1.8}{0.2 \times 10^{-20}} \right)$$

$$= -0.70 \text{ V} - \frac{0.059}{2} [\log 9 + \log 10^{20}]$$

= -0.70 V -
$$\frac{20.059}{2}$$
 [2 log 3 + 20] $\left(\frac{\text{Take } 0.059 \approx 0.06}{\text{log } 3 \approx 0.48} \right)$

$$=-0.70 \text{ V} - 0.03 [2 \times 0.48 + 20]$$

$$=-0.70 \text{ V} - 0.03 \times 20.96$$

$$= (-0.7 - 0.6288) \text{ V} = -1.328 \text{ V}$$

$$\therefore \text{ Hence, } E_{(AsO_4^{3-}|AsO_2^{\odot})} = -1.328 \text{ V}$$

ILLUSTRATION 3.18

Calculate the potential of the following cell:

$$\Pr(s) \begin{vmatrix} Ce^{3+} & (2M), & Cr^{3+} & (1M), \\ Ce^{4+} & (1M) & Cr_2O_7^{2-} & (2M), H^{\oplus} & (1M) \end{vmatrix} \Pr(s)$$

Given:
$$E^{\odot}_{\text{Ce}^{3+}|\text{Ce}^{4+}} = -1.7 \text{ V}, E^{\odot}_{\text{Cr}_2\text{O}_7^{2-}|\text{Cr}^{3+}} = 1.3 \text{ V}$$

 $(\text{Take } 0.059 \approx 0.06)$

$$E^{\Theta}_{\text{Ce}^{3+}|\text{Ce}^{4+}} = -1.7 \text{ V}$$

(Standard oxidation potential value).

So,
$$E^{\odot}$$
 (Ce⁴⁺ | Ce³⁺) = 1.7 V (Geometrical value).

and
$$E^{\odot}_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+})} = 1.3 \text{ V}$$

(Standard reduction potential value).

Anode reduction:

:
$$6Ce^{3+} (2 M) \longrightarrow 6Ce^{4+} (1 M) + 6e^{4}$$

Cathode reaction:

14H^{$$\oplus$$} (1 M) + Cr₂O₇²⁻ (2 M) + $6e^{-}$ \longrightarrow 2Cr³⁺ (1 M) + 7H₂O

Cell reaction:

6Ce³⁺ (2 M) + 14H[⊕] (1 M) + Cr₂O₇²⁻ (2 M)
$$\longrightarrow$$

. 6Ce⁴⁺ (1 M) + 2Cr³⁺ (1 M) + 7H₂O

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{c} - (E^{\odot}_{\text{reduction}})_{a}$$

$$= 1.3 \text{ V} - 1.7 \text{ V} = -0.4 \text{ V}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.06}{6} \log \frac{\left[\text{Ce}^{4+}\right]^{6} \left[\text{Cr}^{3+}\right]^{2}}{\left[\text{Ce}^{3+}\right]^{6} \left[\text{H}^{\oplus}\right]^{14} \left[\text{Cr}_{2}\text{O}_{7}^{2-}\right]}$$

$$= -0.4 \text{ V} - 0.01 \log \frac{(1)^{6} (1)^{2}}{(2)^{6} (1)^{14} (2)}$$

$$= -0.4 \text{ V} - 0.01 (\log 2^{-7})$$

$$= -0.4 \text{ V} - 0.01 (-7 \log 2)$$

$$= (-0.4 + 0.01 \times 7 \times 0.3) \text{ V}$$

$$= (-0.4 + 0.021) \text{ V} = -0.379 \approx -0.38 \text{ V}$$

ILLUSTRATION 3.19

Explain the construction and working of Westron standard cell.

Sol. Westron cell consists of an H-shaped glass vessel with two platinum leads in its two arms at the bottom.

The positive electrode is mercury covered with a paste of mercurous sulphate (Hg₂SO₄) and Hg. The negative electrode consists of Cd-Hg amalgam containing 12% to 24% Cd by weight. Some crystals of 3CdSO₄·8H₂O are kept over the electrodes and the remaining portion is filled with a saturated solution of CdSO₄. The ends are then sealed. This is represented as:

Westron cells are reversible and are not damaged by the passage of current through it. Their EMF does not vary much with the change in temperature.

The reversible reaction that occurs in the cell during its operation is:

Anode reaction (from amalgam):

Cd(s)
$$\longrightarrow$$
 Cd²⁺ + 2e⁻
[$E^{\odot}_{(Cd^{2+}|Cd)} = -0.403 \text{ V}$]

Cathode reaction:

Hg₂SO₄(s) + 2
$$e^- \longrightarrow 2$$
Hg(l) + SO₄²-
[$E^{\odot}_{\text{Hg}_2\text{SO}_4|2\text{Hg}}$] = 0.6153 V

Cell reaction:

$$Cd(s) + Hg_2SO_4(s) \longrightarrow Cd^{2+} + 2Hg(l) + SO_4^{2-}$$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{c}} - (E^{\odot}_{\text{reduction}})_{\text{a}}$$

= 0.6153 V - (-0.403) = 1.0183 V.

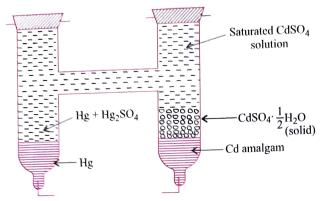


Fig. 3.5 Westron standard cell

Since the activities of element and solid substance $(Cd - Hg_2SO_4)$ and mercury are unity and $[Cd^{2+}]$ and $[SO_4^{2-}]$ in saturated solution are constant and the standard potential of $Cd \mid Cd^{2+}$ and the standard potential of Hg, $Hg_2SO_4 \mid SO_4^{2-}$ are also constant, the E_{cell} is constant (=1.0183 V) at 298 K.

ILLUSTRATION 3.20

The EMF of Westron standard cell is 1.0153 at 20°C and 1.01807 at 25°C. Calculate ΔG , ΔH , and ΔS for the cell reaction at 25°C.

Sol. For Westron cadmium cell, $n_{\text{cell}} = 2$.

$$\left(\frac{\partial E}{\partial T}\right)_{P} = \frac{(1.01807 - 1.01530)}{(298 - 293)} = 5.54 \times 10^{-4} \text{ V deg}^{-1}$$

$$\Delta S = n F \left(\frac{\partial E}{\partial T}\right)_{P}$$

$$= 2 \times 96500 \text{ C} \times 5.54 \times 10^{-4} \text{ V deg}^{-1}$$

$$= 106.9 \text{ J deg}^{-1} = 106.9 \times 10^{-3} \text{ kJ deg}^{-1}$$

$$\Delta G = -nFE = -2 \times 96500 \times 1.01807 \text{ (at 25°C)}$$

$$= -196.45 \text{ kJ mol}^{-1}$$

$$\Delta H = -\Delta G + T \Delta S$$

$$= -196.45 \text{ kJ} + 298 \times 106.9 \times 10^{-3} \text{ kJ mol}^{-1}$$

$$= -196.45 + 31.85 = -164.6 \text{ kJ mol}^{-1}$$

$$\Delta H = nF \left[T \left(\frac{\partial E}{\partial T}\right)_{P} - E \right]$$

$$= 2 \times 96500 [298 \times 5.54 \times 10^{-4} - 1.01807]$$

$$= -164.58 \text{ kJ mol}^{-1} \approx -164.6 \text{ kJ mol}^{-1}$$

ILLUSTRATION 3.21

The EMF of the cell:

$$Cd \mid CdCl_2$$
 (solution) (1 atm) $\mid AgCl$ (s) $\mid Ag$ is 0.675 at 25°C. The temperature coefficient of the cell is -6.5×10^{-4} degree⁻¹. Find the change in heat content and entropy for the electrochemical reaction that occurs when 1 F of electricity is drawn for it.

Sol.
$$E_{\text{cell}} = 0.675 \text{ V}$$

Cell reaction is:

Anode reaction

$$\frac{1}{2}\operatorname{Cd}(s) \longrightarrow \frac{1}{2}\operatorname{Cd}^{2+}(\operatorname{aq}) + e^{-}$$

Cathode reaction:

$$AgCl(s) + e^{-} \longrightarrow Ag(s) + Cl^{\ominus}(aq)$$

Cell reaction:

$$\frac{1}{2}\operatorname{Cd}(s) + \operatorname{AgCl} \Longrightarrow \operatorname{Ag}(s) + \frac{1}{2}\operatorname{Cd}^{2+}(\operatorname{aq}) + \operatorname{Cl}_{\operatorname{aq}}$$

Temperature coefficient of the cell, i.e.,

$$\left(\frac{\partial E}{\partial T}\right)_{P} = -6.5 \times 10^{-4} \text{ V deg}^{-1}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T}\right)_{P} \qquad (n_{\text{cell}} = 1)$$

$$= 1 \times 96500 \times (-6.5 \times 10^{-4})$$

$$= -65.73 \text{ V deg}^{-1}$$

$$E = -\frac{\Delta H}{nF} + T \left(\frac{\partial E}{\partial T}\right)_{P}$$

$$0.675 \text{ V} = \frac{-\Delta H}{1 \times 96500} + 298 (-6.5 \times 10^{-4})$$

$$\Delta H = -83829.55 \text{ J} \approx -83.83 \text{ kJ mol}^{-1}$$

ILLUSTRATION 3.22

At 25°C, the free energy of formation of $H_2O(1)$ is – 56,700 Cal mol^{-1} . The free energy of ionization of water to H^{\oplus} and OH^{\otimes} 19050 cal mol^{-1} . What is the reversible EMF of the following cell at 25°C:

 $H_2(g)$ (1 atm) $\left| H^{\oplus} \right| \left| \begin{array}{c} \odot \\ OH, O_2(g), 1 \text{ atm} \end{array} \right|$

Sol. Given:

$$H_2(g) + \frac{1}{2}O_2(g) \iff H_2O(l)$$
 ...(i)

$$H_2O \rightleftharpoons H^{\oplus} + OH$$

 $\Delta G_1 = -56,700 \text{ cal mol}^{-1}, \Delta G_2 = 19050 \text{ cal mol}^{-1}$ Cell reaction

$$H_2 \Longrightarrow 2H^{\oplus} + 2e^{-}$$

...(ii)

$$\frac{1}{2}O_2 + H_2O + 2e^- \implies 2OH$$

$$H_2 + \frac{1}{2}O_2 + H_2O \implies 2H^{\oplus} + 2OH$$

Multiply Eq. (ii) by 2 and adding Eq. (i), we get

$$H_2 + \frac{1}{2}O_2 + H_2O \implies 2H^{\oplus} + 2OH$$

$$\Delta G = \Delta G_1 + 2\Delta G_2$$
= -56700 + 2 × 19050

= -18600 cal mol⁻¹

= -18600 × 4.2 J mol⁻¹ (1 cal = 4.184 J ≈ 4.2 J)

= -78120 J mol⁻¹

$$\Delta G = -nFE_{cell}$$
- 78120 J mol⁻¹ = - 2 × 96500 C × E_{cell}

$$\therefore E_{cell} = 0.405 V$$

ILLUSTRATION 3.23

Find K_c for the complex:

$$\frac{\operatorname{Ad} A_{c} \operatorname{IO} \operatorname{IO}}{[\operatorname{Ag}(\operatorname{NH}_{3})_{2}]^{\oplus}} \Longrightarrow \operatorname{Ag}^{\oplus} + 2\operatorname{NH}_{3}$$

$$E_{(Ag^{\oplus}/Ag)}^{\ominus} = 0.8 \text{ V and } E_{[Ag(NH_3)_2]^{\oplus}|Ag|NH_3}^{\ominus} = 0.37 \text{ V}$$

Sol. Anode reaction:

$$Ag \iff Ag^{\oplus} + e^{f}$$

Cathode reaction: $[Ag(NH_3)_2]^{\oplus}$ \Longrightarrow $Ag + 2NH_3$

Cell reaction: $[Ag(NH_3)_2]^{\oplus} \iff Ag^{\oplus} + 2NH_3$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{c}} - (E^{\odot}_{\text{reduction}})_{\text{a}}$$

$$= 0.37 \text{ V} - 0.8 \text{ V} = -0.43 \text{ V}$$

$$\log K_{\rm c} = \frac{n_{\rm cell} \times E_{\rm cell}^{\odot}}{0.059}$$
$$= \frac{1 \times (-0.43 \text{ V})}{0.059} = -7.22$$

$$K_{o}$$
 = Antilog (-7.22)

$$=$$
 Antilog $(-7 - 0.22 + 1 - 1)$

= Antilog (
$$\overline{8}$$
.78) = 6×10^{-8}

ILLUSTRATION 3.24

The standard free energy of formation of AgCl(s) at 25°C is $-109.7 \text{ kJ mol}^{-1}$ and $[H^{\oplus} + \text{Cl}^{\odot}]$ (aq) is $-131.2 \text{ kJ mol}^{-1}$. Find E^{\odot} of a cell made up cells, with standard hydrogen electrode, and Cl^{\odot} | Ag | AgCl(s).

Sol. Anode reaction:
$$\frac{1}{2}H_2(g) \longrightarrow H^{\oplus}(aq) + e^{-}$$

Cathode reaction:

$$AgCl(s) + e^{-} \longrightarrow Ag(s) + Cl^{\odot}(aq)$$

Cell reaction:

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^{\oplus}(aq) + Cl^{\ominus}(aq) + Ag(s)$$

$$\begin{split} & \Delta_{\rm r} G^{\odot} = \Sigma G^{\odot}_{\rm P} - \Sigma G^{\odot}_{\rm R} \\ & = \Delta G^{\odot}_{\rm P} - \Delta G^{\odot}_{\rm R} \\ & = \Delta G^{\odot}_{\rm (H^{\oplus} + Cl^{\odot})} - \Delta G^{\odot}_{\rm (AgCl)} \\ & = -131.2 - (-109.7) = -21.5 \text{ kJ mol}^{-1} \\ & = -nFE^{\odot}_{\rm cell} \end{split}$$

$$E_{\text{cell}}^{\odot} = \frac{-\Delta_{\text{r}} G^{\odot}}{n \text{F}} = \frac{-21.5 \text{ kJ mol}^{-1}}{1 \times 96500 \text{ C}}$$
$$= 0.2228 \approx 0.223 \text{ V}$$

ILLUSTRATION 3.25

The EMF of the following cell is 1.05 V at 25°C:

Pt, H₂(g) (1.0 atm) | NaOH (0.1 M), NaCl (0.1 M) | AgCl(s), Ag(s)

- a. Write the cell reaction,
- **b.** Calculate $pK_{\mathbf{w}}$ of water.

Sol. Anode reaction:
$$\frac{1}{2}H_2(g) \longrightarrow H^{\oplus} + \swarrow$$

Cathode reaction

$$AgCl(s) + \checkmark \longrightarrow Ag(s) + Cl^{\odot}$$

Cell reaction:

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow Ag(s) + Cl^{\ominus} + H^{\oplus}$$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{c}} - (E^{\odot}_{\text{reduction}})_{\text{a}}$$

= 0.23 - 0 = 0.23 V

$$E_{\mathrm{cell}} = E_{\mathrm{cell}}^{\ominus} - \frac{0.059}{n_{\mathrm{cell}}} \log [\mathrm{H}^{\oplus}] [\mathrm{Cl}^{\ominus}]$$

 $[n_{\text{cell}} = 1, \text{ activity of Ag(s) and AgCl(s)} = 1, p_{\text{H}_2} = 1 \text{ atm}]$

$$1.05 \text{ V} = 0.23 - \frac{0.059}{1} \log [\text{H}^{\oplus}] [\text{Cl}^{\odot}]$$

$$\begin{bmatrix} K_{\mathbf{w}} = [\mathbf{H}^{\oplus}] [O\mathbf{H}] \\ \therefore [\mathbf{H}^{\oplus}] [C\mathbf{l}^{\odot}] = \frac{K_{\mathbf{w}} [C\mathbf{l}^{\odot}]}{[O\mathbf{H}]} \end{bmatrix}$$

1.05 V = 0.23 – 0.059 log
$$\frac{K_{w} [Cl^{\odot}]}{[OH]}$$
 $\left[\begin{array}{c} [Cl^{\odot}] = [OH] \\ = 0.1 \text{ M} \end{array} \right]$

1.05 V =
$$0.23 - 0.059 \log \frac{K_{\rm w} \times 0.1 \,\rm M}{0.1 \,\rm M}$$

$$(1.05 - 0.23) \text{ V} = 0.059 [-\log K_{\text{w}}] = 0.059 \text{ p}K_{\text{w}}$$

$$\therefore pK_{\rm w} = \frac{(1.05 - 0.23)}{0.059} = 13.89$$

ILLUSTRATION 3.26

If the oxidation of oxalic acid by acidic MnO_4° solution is carried out in a reversible cell, then what is the electrode reaction and equilibrium constant of the cell reaction.

Given:

$$E^{\odot}_{(MnO_4^{\odot} \mid Mn^{2+})} = 1.51 \text{ V}$$

$$E^{\odot}_{(\text{CO}_2 \mid \text{C}_2\text{O}_4^{2-})} = -0.49 \text{ V}$$

Sol. Anode reaction: $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^{-1} \times 5$

Cathode reaction

de reaction
$$5e + \text{MnO}_4^{\circ} + 8\text{H}^{\oplus} \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}] \times 2$$

Cell reaction:

$$5C_2O_4^{2-} + 2MnO_4^{\odot} + 16H^{\oplus} \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

$$E^{\odot}_{\text{cell}} = (E^{\odot}_{\text{reduction}})_{\text{c}} - (E^{\odot}_{\text{reduction}})_{\text{a}}$$
$$= 1.51 - (-0.49) = 2.0 \text{ V}$$

Cell representation:

Pt,
$$CO_2(g) | H_2C_2O_4, H^{\oplus} | H^{\oplus}, MnO_4^{\odot} | Mn^{2+} | Pt$$

$$A G^{\odot} = -nF F^{\odot}, \quad (n_{col} = 10)$$

$$\Delta_{\rm r} G^{\odot} = -nF E^{\odot}_{\rm cell} (n_{\rm cell} = 10)$$

= -10 × 96500 C × 2.0 V
= -193 × 10⁴ J mol⁻¹

$$\Delta_{\rm r} G^{\odot} = -2.303RT \log K_{\rm c}$$

$$_{-193} \times 10^4 \text{ J mol}^{-1} = -2.303 \times 8.134 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

 $\times \log K_c$

$$\log K_{\rm c} = 338.08$$

$$K_{c} = \text{Antilog} (338.08)$$

$$K_c = 1.2 \times 10^{338}$$

3.8.2 RELATION BETWEEN STANDARD POTENTIAL OF HALF CELLS CONTAINING A METAL IN DIFFERENT OXIDATION STATE

If two half-reactions having potential $E_1^{\,\ominus}$ and $E_2^{\,\ominus}$ are combined to give a third half reaction having a potential $E_3^{\,\ominus}$, then

$$\Delta G_3^{\odot} = \Delta G_1^{\odot} + \Delta G_2^{\odot}$$

$$-n_3 F E_3^{\odot} = -n_1 F E_1^{\odot} - n_2 F E_2^{\odot}$$

$$n_2 E_2^{\odot} = n_1 E_1^{\odot} + n_2 E_2^{\odot}$$

$$E_3^{\odot} = \frac{n_1 E_1^{\odot} + n_2 E_2^{\odot}}{n_2}$$

If equal number of electrons are involved, then

$$E_3^{\odot} = E_1^{\odot} + E_2^{\odot}$$

ILLUSTRATION 3.27

Find the standard electrode potential of $MnO_4^{\odot} | MnO_2$. The standard electrode potentials of $MnO_4^{\odot} | Mn^{2+} = 1.51 \text{ V}$ and $MnO_2 | Mn^{2+} = 1.23 \text{ V}$.

Sol. Given:

i.
$$\operatorname{MnO_4}^{\odot} + 8\operatorname{H}^{\oplus} + 5\operatorname{e}^{-} \longrightarrow \operatorname{Mn}^{2+} + 4\operatorname{H}_2\operatorname{O}^{-} \Delta G_1^{\odot}$$

ii.
$$\operatorname{MnO}_2 + 4\operatorname{H}^{\oplus} + 2\operatorname{e}^- \longrightarrow \operatorname{Mn}^{2+} + 2\operatorname{H}_2\operatorname{O} \int \Delta G_2^{\ominus}$$

Subtracting equations (i) – (ii) give the required equation, i.e.,

$$\mathrm{MnO_4}^{\odot} + 4\mathrm{H}^{\oplus} + 3\mathrm{e}^- \longrightarrow \mathrm{MnO_2} + 2\mathrm{H_2O}] \Delta G_3^{\odot}$$

$$\therefore \Delta G_3^{\odot} = \Delta G_1^{\odot} - \Delta G_2^{\odot}$$
$$-3FE_3^{\odot} = -5FE_1^{\odot} - (-2FE_2^{\odot})$$

(or) Use direct relation:

$$E_{3}^{\odot} = \frac{n_{1}E_{1}^{\odot} - n_{2}E_{2}^{\odot}}{n_{3}}$$

$$= \frac{(5 \times 1.51) \text{ V} - (2 \times 1.23) \text{ V}}{3}$$

$$E_{3}^{\odot} = 1.7 \text{ V}$$

ILLUSTRATION 3.28

In 1 M HClO $_4$ solution, formal potentials for the different stages in the reduction of $MnO_4^{\,\odot}$ are given.

$$MnO_4^{\odot} \xrightarrow{0.564 \text{ V}} MnO_4^{2-} \xrightarrow{2.26 \text{ V}} MnO_2$$

$$MnO_2 \xrightarrow{0.95 \text{ V}} Mn^{+3} \xrightarrow{1.51 \text{ V}} Mn^{2+}$$
.

Calculate the formal potential for the following reactions:

- $a. MnO_4^{\odot} \longrightarrow Mn^{2+}$
- **b.** $\operatorname{MnO_4^{2-}} \longrightarrow \operatorname{Mn}^{2+}$

Sol.

1627		
ΔG is additive	Е	$\Delta G = -nFE$
$MnO_4^{\ominus} + e^- \rightarrow MnO_4^{2-}$	0.564	- 1 × 0.564 F(i)
$\frac{\text{MnO}_4^{2-} + 4\text{H}^{\oplus} + 2e^{-} \rightarrow}{\text{MnO}_4^{2-} + 4\text{H}^{\oplus} + 2e^{-} \rightarrow}$	2.26	-2 × 2.26 F
$MnO_2 + 2H_2O$		= - 4.52 F(ii)
$MnO_2 + 4H^{\oplus} + e^{-} \longrightarrow$	0.95	-1 × 0.95 F(iii)
$Mn^{3+} + 2H_2O$		
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	1.51	$-1 \times 1.51 \text{ F }(iv)$

a. Adding Eqs. (i) to (iv), we get

MnO₄[⊙] + 8H[⊕] + 5e⁻
$$\longrightarrow$$
 Mn²⁺ + 4H₂O
∴ $\Delta G = -(0.564 + 4.52 + 0.95 + 1.51)$ F = -5EF
∴ E = $\frac{7.544}{5}$ = 1.51 V

b. Adding Eqs. (ii) to (iv), we get

MnO₄²⁻ + 8H[⊕] + 4e⁻
$$\longrightarrow$$
 Mn²⁺ + 4H₂O
∴ $\Delta G = -(4.52 + 0.95 + 1.51)F = -4EF$

$$E = \frac{6.98}{4} = 1.745 \text{ V}$$

3.9 CONCENTRATION CELLS

Concentration cells are of two types: electrolytic concentration cells and electrode concentration cells.

3.9.1 ELECTROLYTIC CONCENTRATION CELLS

In these cells, identical electrodes are dipped in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to

of higher concentration to that of lower with the passage of time, the two constants. With the passage of time, the two constants are the same of the With the passage of time, the two concentrations who equal. Thus, at the start, the EMF of the cell is a suppose of the c me two concentrations at the start, the EMF of the cell is maximum and to be equal. Thus, at the start, the EMF of the cell is maximum and the start and the start at the start at the two concentrations. and gradually falls to zero.

of gradient cells in which the electrode is reversible with incontration: report to cation:

$$\frac{e^{ctn}}{a} \frac{(c_1) \| \mathbf{M}^{n+}(c_2) \| \mathbf{M}^{n+}(c_2) \| \mathbf{M}(s)}{\| \mathbf{M}^{n+}(c_2) \| \mathbf{M}(s) \|}$$

a.
$$M(s) \mid M^{*}(c_1) \mid | Zn^{2+}(c_2) \mid Zn(s)$$

b. $Zn(s) \mid Zn^{2+}(c_1) \mid | Zn^{2+}(c_2) \mid | Zn(s)$

b.
$$Zn(s) | Zn^{\Theta}(c_1) | Zn^{\Theta}(c_2) + Zn(s)$$

c. $Pt, H_2(g) (1 \text{ atm}) | H^{\oplus}(c_1) | H^{\oplus}(c_2) | H_2(g) (1 \text{ atm}), Pt$

c. Pt.
$$H_2(g)$$
 (Table 1) $\|Ag^{\oplus}(c_2)\|Ag(s)$
d. $Ag(s)\|Ag^{\oplus}(c_1)\|Ag^{\oplus}(c_2)\|Ag(s)$

ioncentration cells in which the electrode is reversible with napect to anion:

 $_{\mathbf{a.}}\operatorname{Pt,Cl}_{2}(\mathbf{g})\text{ (1 atm)}\mid\operatorname{Cl}^{\circleddash}(c_{1})\parallel\operatorname{Cl}^{\circleddash}(c_{2})\mid\operatorname{Cl}_{2}(\mathbf{g})\text{ (1 atm), Pt.}$ The two half reactions are as follows:

$$M(s) \longrightarrow M^{n+}(c_1) + me$$

Cathode reaction:
$$M^{n+}(c_2) + ne^- \longrightarrow M(s)$$

$$M^{n+}(c_2) \longrightarrow M^{n+}(c_1)$$

Note: For concentration cell, $E_{cell}^{\ominus} = 0 \text{ V}$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{n_{\text{cell}}} \log Q_{\text{cell}}$$

$$= 0 - \frac{0.059}{n_{\text{cell}}} \log \frac{[M^{n+}(c_1)]}{[M^{n+}(c_2)]}$$

$$= -\frac{0.059}{n_{\text{cell}}} \log \frac{[M^{n+}(c_1)]}{[M^{n+}(c_2)]}$$

In general,
$$E_{\text{cell}} = -\frac{0.059}{n_{\text{cell}}} \log \frac{c_1}{c_2}$$
 (if electrode is reversible

with respect to cation). The cell reaction is spontaneous in forward direction when c_2 (RHS) > c_1 (LHS) or cell is said to be exergonic [le,, ΔG = -ve). Cell is nonspontaneous when c_2 (RHS) < c_1 (LHS) or cell is said to be endergonic (i.e., $\Delta G = +ve$).

EMF of Concentration Cell Made by Using Hydrogen Electrode

Cell representation:

$$\mathsf{Pt}, \mathsf{H}_{2}(\mathsf{g}) \ (1 \ \mathsf{atm}) \ | \ \mathsf{H}^{\oplus}(c_{1}) \ | \ \mathsf{H}^{\oplus} \ (c_{2}) \ | \ \mathsf{H}_{2}(\mathsf{g}) \ (1 \ \mathsf{atm}), \ \mathsf{Pt}$$

$$H_2(g) \longrightarrow 2H^{\oplus}(c_1) + 2e^{-c_1}$$

Cathode reaction:
$$2H^{\oplus}(c_2) + 2e \longrightarrow H_2(g)$$

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$$2H^{\oplus}(c_2) \longrightarrow 2H^{\oplus}(c_1)$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log \frac{\left[H^{\oplus}(c_1)\right]^2}{\left[H^{\oplus}(c_2)\right]^2}$$

$$= 0 - \frac{0.059}{2} \times 2 \left[\log H^{\oplus}(c_1) - \log H^{\oplus}(c_2)\right]$$

$$= -0.059 \left[pH(c_2) - pH(c_1)\right]$$

In general, E_{cell} of hydrogen electrode is:

$$E_{\text{cell}} = -0.059 \text{ (pH}_{\text{cathode}} - \text{pH}_{\text{anode}})$$
or
$$= 0.059 \text{ (pH}_{\text{anode}} - \text{pH}_{\text{cathode}})$$

3.9.2 ELECTRODE CONCENTRATION CELLS

In these cells the potential difference is developed between two similar electrodes at different concentration immersed in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressure in the same solution of hydrogen ion constitute a cell of the following type:

$$Pt, H_2(g)(p_1) | HC1 (1 M) | H_2(g) (p_2), Pt$$

$$H_2(g)(p_1) \longrightarrow 2H^{(g)}(1M) + 2e^{-\frac{1}{2}}$$

Cathode reaction:
$$2H^{\oplus}(1 \text{ M}) + 2e^{-} \longrightarrow H_2(g)(p_2)$$

Cell reaction:
$$H_2(g)(p_1) \longrightarrow H_2(g)(p_2)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{p_2}{p_1}$$

$$= 0 - \frac{0.059}{2} \log \frac{p_2}{p_1}$$

$$= -\frac{0.059}{2} \log \frac{p_2}{p_1}$$

$$= \frac{0.059}{2} \log \frac{p_1}{p_2}$$

The concentration cell is spontaneous or feasible or exergonic $(\Delta G = -ve)$, in forward direction if p_1 (LHS) $> p_2$ (RHS).

EMF of the Concentration Cell Formed by Coupling an Electrolytic and Electrode Concentration Cell

The cell representation of a concentration cell made by using hydrogen electrode is as follows:

Pt,
$$H_2(p_1 \text{ atm}) \mid H^{\oplus}(M_1) \parallel H^{\oplus}(M_2) \parallel H_2(p_2 \text{ atm})$$

Anode reaction:

$$H_2(p_1 \text{ atm}) \longrightarrow 2H^{\oplus}(M_1) + 2e^{-1}$$

Cathode reaction:

$$2H^{\oplus}(M_2) + 2e^{-} \longrightarrow H_2(p_2 \text{ atm})$$

Cell reaction:

$$\frac{H_2(p_1 \text{ atm}) + 2H^{\oplus}(M_2) \longrightarrow H_2(p_2 \text{ atm}) + 2H^{\oplus}(M_1)}{0.059 \qquad (p_{W_1}) \text{ archiv} [H^{\oplus}]^2 \text{ arch}}$$

$$E_{\text{cell}} = E^{\bigcirc}_{\text{cell}} - \frac{0.059}{2} \log \frac{(p_{\text{H}_2})_{\text{cathode}} [\text{H}^{\oplus}]^2_{\text{anode}}}{(p_{\text{H}_2})_{\text{anode}} [\text{H}^{\oplus}]^2_{\text{cathode}}}$$

$$= 0 - \frac{0.059}{2} \log \frac{\left[H^{\oplus}\right]^{2}_{\text{anode}}}{\left[H^{\oplus}\right]^{2}_{\text{cathode}}} - \frac{0.059}{2} \log \frac{(p_{\text{H}_{2}})_{\text{cathode}}}{(p_{\text{H}_{2}})_{\text{anode}}}$$

$$= -0.059 \left(pH_{cathode} - pH_{anode} \right) - \frac{0.059}{2} \log \frac{(p_{H_2})_{cathode}}{(p_{H_1})_{anode}}$$

$$= 0.059 \left[(pH_{anode} - pH_{cathode}) + \frac{1}{2} log \frac{(p_{H_2})_{anode}}{(p_{H_2})_{cathode}} \right]$$

ILLUSTRATION 3.29

Find the EMF of the concentration cell represented as given below:

$$\underbrace{\frac{\text{Pt. H}_2(2\text{ atm}) \, | \, \text{H}_2\text{SO}_4(0.01\text{M})}_{\text{Anode}} \Big| \underbrace{\frac{\text{HCl}(0.1\text{M}) | \, \text{H}_2(1\text{ atm}), \, \text{Pt}}_{\text{Cathode}}}_{\text{Cathode}}$$

Sol. E_{cell} will be positive only when

$$[\mathbf{H}^{\oplus}]_{\mathrm{cathode}} \ge [\mathbf{H}^{\oplus}]_{\mathrm{anode}}$$
 and $(p_{\mathrm{H_2}})_{\mathrm{anode}} \ge (p_{\mathrm{H_2}})_{\mathrm{cathode}}$

So in the above case, $E_{\rm cell}$ will be positive, and cell will be spontaneous or feasible or exergonic.

$$[H^{\oplus}]_{anode} = 2 \times 0.01 \text{ M} = 2 \times 10^{-2} \text{ N}$$

$$(n \text{ factor for H}_2\text{SO}_4 = 2)$$

$$pH_{anode} = -\log (2 \times 10^{-2}) = 2 - 0.3 = 1.7$$

$$[H^{\oplus}]_{cathode} = 1 \times 0.1 \text{ M} \qquad (n \text{ factor for HCl} = 1)$$

$$pH_{cathode} = -\log (10^{-1}) = 1$$

Use the relation,

$$E_{\text{cell}} = 0.059 \left[(\text{pH}_{\text{anode}} - \text{pH}_{\text{cathode}}) + \frac{1}{2} \log \frac{(p_{\text{H}_2})_{\text{anode}}}{(p_{\text{H}_2})_{\text{cathode}}} \right]$$

$$= 0.059 \left(1.7 - 1 + \frac{1}{2} \log \frac{2 \text{ atm}}{1 \text{ atm}} \right) = 0.059 \left(0.7 + \frac{1}{2} \log 2 \right)$$

$$= 0.059 \left(0.7 + \frac{1}{2} \times 0.3 \right) = 0.059(0.7 + 0.15)$$

$$= 0.059 \times 0.85 \approx 0.06 \times 0.85 = 0.05 \text{ V}$$

ILLUSTRATION 3,30

Calculate the EMF of the following concentration cells at 30°C and predict whether the cells are exergonic or endergonic. [Assume Kw does not change at 30°C]

- **a.** Pt | $H_2(g)$ (1 atm) | $H^{\oplus}(10^{-6} \text{ M}) \parallel H^{\oplus}$ (10⁻⁴ M) | $H_2(g)$ (1 atm) | Pt
- **b.** Pt | H₂(g) (1 atm) | NaOH (10⁻⁴ M) || H $^{\oplus}$ (10⁻⁵ M) | H₂(g), (1 atm) | Pt
- **c.** Pt \mid H₂(g) (1 atm) \mid H₂SO₄ (0.05 M) \parallel KOH (10⁻³ M) \mid H₂(g) (1 atm) \mid Pt
- **d.** Pt | H₂(g) (1 atm) | CH₃COOH (10^{-2} M) || CsOH (10^{-3} M) | H₂(g) (1 atm) | Pt (p K_a of CH₃ COOH = 4.74)
- e. Pt $| H_2(g) (1 \text{ atm}) | H_2O | | HCl (10^{-3}\text{M}) | H_2(g) (1 \text{ atm}) | Pt$

f.
$$|Pt| |H_2(g)| NH_4OH (10^{-2}M) |RbOH| |H_2(g)| Pt |RbOH| |R$$

g. Pt
$$H_2(g)$$
 CH_3COONa $NH_4CI(0.4M)$ $H_2(g)$ Pt $(1atm)$ $+$ NH_4OH $(0.2M)$ pK_b of NH_4OH $= 4.74$

Note: At 30°C, the value of $2.303 \frac{RT}{F} \approx 0.06$.

Sol.

a. $[H^{\oplus}]_{\text{cathode}} > [H^{\oplus}]_{\text{anode}}$ or $pH_{\text{cathode}} < pH_{\text{anode}}$ So EMF of the cell will be positive and the cell will be spontaneous or exergonic (i.e., $\Delta G = -ve$). $(pH)_c = 4$, $(pH)_a = 6$

 $E_{cell} = -0.060 \text{ (pH}_{c} - \text{pH}_{a}) = -0.060 \text{ (4-6)} = 0.12 \text{ (pH)}_{c} = 5, \text{ (pOH)}_{a} = 4, \text{ or (pH)}_{a} = 14 - 4 = 10$ Since (pH)_c < (pH)_a, so EMF of the cell will be positive and the cell will be spontaneous or exergonic.

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}}) = -0.06(5 - 10) = 0.30 \text{ y}$$

c. Since $[H_2SO_4] = [H^{\oplus}]_a = 0.05 \times 2 (n \text{ factor})$ = 0.1 N = 10⁻¹ N pH_a = 1, (pOH)_c = 3, pH_c = 14 - 3 = 11

Since $pH_c > pH_a$, so EMF of cell will be negative and the cell will not be feasible or non-spontaneous or endergonic (i.e., $\Delta G = +ve$).

$$E_{\text{cell}} = -0.06(\text{pH}_{\text{c}} - \text{pH}_{\text{a}}) = -0.06(11 - 1) = -0.6 \text{ V}.$$

d. CH₃COOH is weak acid and CsOH is a strong base.

Thus, pH_{wA} =
$$\frac{1}{2}$$
 (pK_a - log c)
= $\frac{1}{2}$ (4.74 - log 10⁻²)
= $\frac{1}{2}$ (4.74 + 2) = 3.37 = pH_a

$$(pOH)_c = 3, \Rightarrow pH_c = 14 - 3 = 11$$

Since $pH_c > pH_a$, so EMF of cell will be negative and is endergonic.

$$E_{\text{cell}} = -0.06 \text{ (pH}_{c} - \text{pH}_{a}) = -0.06 \text{ (11 - 3.37)}$$

= -0.06×7.63
= -0.457 V

e. pH of $H_2O = 7 = pHa$ $pH_c = 3$ Since pH < pH EMF y = +y

Since $pH_c < pH_a$, $EMF_{cell} = +ve$, cell is exergonic.

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}}) = -0.06 \text{ (3 - 7)} = 0.24 \text{ V}$$

f. NH₄OH is a weak base and RbOH is a strong base.

Thus, pOH_{W_B} =
$$\frac{1}{2}$$
 (pK_b - log C) = $\frac{1}{2}$ (4.74 - log 10⁻²)
= 3.37

 $pH_a = 14 - 3.37 = 10.63$ $(pOH)_c = 3$, $\Rightarrow pH_c = 14 - 3 = 11$ Since $pH_c > pH_a$, therefore, $EMF_{cell} = -ve$, $cell \ will \ be$

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}}) = -0.06 \text{ (11 - 10.63)}$$

= -0.022 V

g. Mixture of CH_3COOH (W_A) and salt of W_A/S_B (CH_3COONa) is an acidic buffer. Thus,

$$\therefore pH_{acid buffer} = pK_a + log \frac{[Salt]}{[Acid]}$$

$$= 4.74 + \log \frac{10^{-1} \text{ M}}{10^{-2} \text{ M}}$$
$$= 4.74 + 1 = 5.74$$

Mixture of $NH_4OH(W_B)$ and salt of W_B/S_A (NH_4CI) is a basic buffer.

a basic buffer
$$= pK_a + log \frac{[Salt]}{[Base]}$$

$$= 4.74 + log \frac{0.4 \text{ M}}{0.2 \text{ M}}$$

$$= 4.74 + log 2$$

$$= 4.74 + 0.3 = 5.04$$

$$pH_c = 14 - 5.04 = 8.96$$

 $_{Since pH_c} > pH_a,$

 $\therefore EMF_{cell} = -ve$, cell is endergonic.

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}}) = -0.06 \text{ (8.96} - 5.74)$$

= -0.06×3.22
= -0.1932 V

ILLUSTRATION 3.31

Calculate the EMF of the following concentration cells at 30°C and predict whether the cells are exergonic or endergonic.

c. Pt
$$H_2(g)$$
 CH_3COOH $NH_4OH(10^{-2} M)$ $H_2(g)$, Pt $pK_b = 4.74$ $pK_b = 4.74$ (1 atm)

d.
$$Ag(s) | Ag^{\oplus}(0.1 \text{ M}) || Ag^{\oplus}(1 \text{ M}) | Ag(s)$$

e. Pt
$$\left| \frac{\text{Cl}_2(g)}{(1 \text{ atm})} \right| \frac{\text{Cl}^{\ominus}(10^{-3} \text{M})}{\left| \frac{\text{Cl}^{\ominus}(10^{-2} \text{M})}{(1 \text{ atm})} \right|} \frac{\text{Cl}_2(g)}{(1 \text{ atm})} \right| \text{Pt}$$

f. Pt
$$Cl_2(g)$$
 $Cl^{\odot}(10^{-3}M)$ $Cl_2(g)$ $Cl_2(g)$

Sol. Note that at 30°C, the value of $2.303 \frac{RT}{F} = 0.06$.

a. CH₃COONa is a salt of W_A/S_B. Thus

$$pH_a = \frac{1}{2} (pK_w + pK_a + \log c)$$
$$= \frac{1}{2} (14 + 4.74 + \log 10^{-2})$$
$$= \frac{1}{2} (14 + 4.74 - 2) = 8.37$$

∴ pH_a = 8.37
NH₄NO₃ is a salt of W_B/S_A. Thus,
pH_c =
$$\frac{1}{2}$$
 (pK_w - pK_b - log c)
= $\frac{1}{2}$ (14 - 4.74 - log 0.2)

$$= \frac{1}{2} (14 - 4.74 - \log 0.2)$$

$$= \frac{1}{2} [14 - 4.74 - \log 2 \times 10^{-1}]$$

$$= \frac{1}{2} (14 - 4.74 - 0.3 + 1) = 4.98.$$

Since $pH_c < pH_a$, therefore, $EMF_{cell} = +ve$ and the cell will be exergonic.

will be exergonic.

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}}) = -0.06 \text{ (4.98} - 8.37)$$

 $= -0.06 \times -3.39$
 $= 0.2034 \text{ V}$

b. CH_3COONH_4 is salt of W_A/W_B and its pH is independent of the concentration.

$$pH_{a} = \frac{1}{2} (pK_{w} + pK_{a} - pK_{b})$$

$$= \frac{1}{2} (14 + 4.74 - 4.74) = 7$$

CH₃COONa is a salt of W_A/S_B.

$$\therefore pH_c = \frac{1}{2} (pK_w + pK_a + \log c)$$

$$= \frac{1}{2} (14 + 4.74 + \log 10^{-3}) = 7.87$$

Since $pH_c > pH_a$

 \therefore EMF_{cell} = -ve and the cell will be endergonic

$$E_{\text{cell}} = -0.06 \text{ (pH}_{c} - \text{pH}_{a}) = -0.06 \text{ (7.87} - 7)$$

$$= -0.06 \times 0.87$$

$$= 0.0522 \text{ V}$$

c. CH₃COOH is a weak acid (W_A).

Thus, pH_{WA} =
$$\frac{1}{2}$$
 (pK_a - log c)
= $\frac{1}{2}$ (4.74 - log 10⁻¹) = 2.87

 NH_4OH is a weak base (W_B) .

Thus, pOH_{W_B} = (pOH)_c =
$$\frac{1}{2}$$
 (pK_b - log c)
= $\frac{1}{2}$ (4.74 - log 10⁻²)
= 3.37

Thus, $pOH_{W_R} = pH_c = 14 - 3.37 = 10.63$

Since $pH_c > pH_a$, therefore, $EMF_{cell} = -ve$, and the cell will be endergonic.

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}}) = -0.06 \text{ (10.63} - 2.87)$$

= -0.06×7.67
= -0.4656 V

 $Ag(s) \longrightarrow Ag^{\oplus}(0.1 \text{ M}) + e^{-t}$ d. Anode reaction:

 $Ag^{\oplus}(1 M) + \swarrow \longrightarrow Ag(s)$ Cathode reaction:

 $\overline{Ag^{\oplus}(1 M)} \longrightarrow Ag^{\oplus}(0.1 M)$ Cell reaction:

Since $[Ag^{\oplus}]_c > [Ag^{\oplus}]_a$, therefore, $EMF_{cell} = +ve$ and the cell will be exergonic.

the cell will be exerged.
$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.06}{n_{\text{cell}}} \log \frac{[Ag^{\oplus}]_a}{[Ag^{\oplus}]_c}$$

$$= 0 - \frac{0.06}{1} \log \frac{0.1 \text{ M}}{1 \text{ M}}$$

$$E_{\text{cell}} = -0.06 [\log 10^{-1}] = -0.06 \times -1 = 0.06 \text{ V}$$

e. Anode reaction:

Anode reaction:

$$2 \text{ Cl}^{\odot} (10^{-3} \text{ M}) \longrightarrow \text{ Cl}_{2}(g) (1 \text{ atm}) + 2e^{-1}$$

Cathode reaction:

cl₂(g) (
$$1atm$$
) + $2e$ $\longrightarrow 2Cl^{\odot} (10^{-2} \text{ M})$

Cell reaction:

$$2 \text{ Cl}^{\odot} (10^{-3} \text{ M}) \longrightarrow 2 \text{Cl}^{\odot} (10^{-2} \text{ M})$$

Since $[Cl^{\odot}]_c > [Cl^{\odot}]_a$,

Therefore, $EMF_{cell} = -ve$ and the cell will be endergonic.

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.06}{n_{\text{cell}}} \log \frac{[\text{Cl}^{\odot}]_{\text{c}}^{2}}{[\text{Cl}^{\odot}]_{\text{a}}^{2}}$$

$$= 0 - \frac{0.06}{2} \log \frac{(10^{-2})^{2}}{(10^{-3})^{2}}$$

$$= -\frac{0.06}{2} \times 2 \log 10 = -0.06 \text{ V}$$

Note: In case of negative ion, e.g., Cl[⊕] ion, EMF_{cell} is positive when $[M^{x-}]_c < [M^{x-}]_a$, and $(p_2)_c > (p_1)_a$ whereas in case of positive ion, e.g., Ag^{\oplus} ion, it is reversed, i.e., when $[M^{x+}]_c >$ $[M^{x+}]_a$, and $(p_1)_a > (p_2)_c$ the EMF_{cell} is positive.

f. Anode reaction:

$$2Cl^{\ominus}(10^{-3} \text{ M}) \longrightarrow Cl_2(g)(2 \text{ atm}) + 2e^{-2g}$$

Cathode reaction:

$$Cl_2(g)$$
 (1 atm) + $2e^- \longrightarrow 2Cl^{\odot}$ (10⁻² M)

Cell reaction: $2Cl^{\odot} (10^{-3} \text{ M}) + Cl_2(g) (1 \text{ atm}) \longrightarrow$ $2Cl^{\odot} (10^{-2} \text{ M}) + Cl_{2}(g) (2 \text{ atm})$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.06}{n_{\text{cell}}} \log \frac{[\text{CI}^{\circ}]_{c}^{2} [p_{\text{Cl}_{2}}]_{a}}{[\text{CI}^{\circ}]_{a}^{2} [p_{\text{Cl}_{2}}]_{c}}$$

$$= 0 - \frac{0.06}{2} \log \frac{(10^{-2})^{2} \times 2 \text{ atm}}{(10^{-3})^{2} \times 1 \text{ atm}}$$

$$= -\frac{0.06}{2} [\log 10^{2} \times 2]$$

$$= -\frac{0.06}{2} [2 \log 10 + \log 2]$$

$$= -0.03 [2 + 0.3] = -0.03 \times 2.3 = -0.069 \text{ V}$$

Therefore, EMF_{cell} is negative and the cell will be

 $\mathrm{EMF_{cell}}$ is positive, if $\mathrm{[Cl^{\odot}]_a} > \mathrm{[Cl^{\odot}]_c}$ and $\mathrm{(p_{Cl,)_c}} >$ $(p_{\text{Cl}})_{\text{a}}$

ILLUSTRATION 3.32

The EMF of the following cell is 0.180 V at 30°C.

The EMF of the following
$$Pt(s) | H_2(g) | HA$$

$$| H_2(g) | HA | (1.00 \text{ mL}, 0.1 \text{ M}) | H_2SO_4 | H_2(g) | Pt(s)$$

Find EMF_{cell} when

- a. 40 mL of 0.2 M NaOH is added to the negative terminal of the battery.
- b. 50 mL of 0.2 M NaOH is added to the negative terminal of the battery.
- c. 50 mL of 0.2 M NaOH is added to 100 mL of H₂SO₄ at the positive terminal of the battery.

Sol. It is an electrolytic concentration cell.

Note: The value of $2.303 \frac{RT}{F} = 0.06$ at 30°C.

$$[H_2SO_4] = 0.05 \text{ M} = 0.05 \times 2 \text{ (n factor)}$$

$$= 0.1 \text{ N} = 10^{-1} \text{ N}$$

$$pH_c = -\log (10^{-1} \text{ N}) = 1$$

$$pH_a = ?$$

$$E_{cell} = -0.06 (pH_c - pH_a) = -0.06 (1 - pH_a)$$

$$0.180 \text{ V} = -0.06 (1 - pH_a)$$

$$pH_a = \frac{0.180}{0.06} + 1 = 4$$

$$\therefore [H^{\oplus}]_a = 10^{-4} \text{ M}$$

Since HA is a weak acid (W_{Δ}) ,

$$pH_{a} = pH_{wA} = \frac{1}{2} (pK_{a} - \log C)$$

$$4 = \frac{1}{2} (pK_{a} - \log 10^{-1})$$

$$\therefore pK_a = 7$$

a. When 40 mL of 0.2 M NaOH (= $40 \times 0.2 = 8 \text{ mmol})$ is added to a weak acid, acidic buffer is formed.

Total volume = 100 + 40 = 140 mL

$$[Salt] = [NaA] = \frac{8 \text{ mmol}}{140 \text{ mL}}$$

$$[W_{\rm A}]_{\rm left} = [{\rm HA}]_{\rm left} = \frac{2 \text{ mmol}}{140 \text{ mL}}$$

$$pH_{a} = pH_{acidic buffer} = pK_{a} + log \frac{[Salt]}{[Acid]}$$
$$= 7 + log \left(\frac{8/140}{2/140}\right)$$
$$= 7 + log 2^{2}$$
$$= 7 + 2 \times 0.3 = 7.6$$

Thus,

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}})$$

 $= -0.06 \text{ (1 - 7.6)}$
 $= -0.06 \times -6.6 = 0.396 \text{ V}$

b. When 50 mL of 0.2 M NaOH (= $50 \times 0.2 = 10$ mmol) is added to weak acid (HA), salt of W_A/S_B (NaA) is formed.

HA + NaOH
$$\longrightarrow$$
 NaA + H₂O

Initial 100 × 0.1 10 mmol 0 0

Final 10 - 10 (10 - 10) 10 m mol

conc. = 0 = 0

$$[NaA] = \frac{10 \text{ mmol}}{150 \text{ mL}} = \frac{1}{15} \text{M}$$

Thus, pH of a salt of W_A/S_B is given by:

$$_{pH_a} = pH_{saltW_A/S_B} = \frac{1}{2} (pK_w + pK_a + \log C)$$

 $[pK_a \text{ of HA} = 7, \text{ from part (a) above}]$

$$pH_a = \frac{1}{2} \left(14 + 7 + \log \frac{1}{15} \right)$$

$$= \frac{1}{2} (21 + \log 1 - \log 15]$$

$$= \frac{1}{2} (21 + 0 - \log 3 - \log 5)$$

$$= \frac{1}{2} (21 - 0.48 - 0.7) = 9.91$$

Thus

$$E_{\text{cell}} = -0.06 \text{ (pH}_{c} - \text{pH}_{a})$$

= $-0.06 \times (1 - 9.91)$
= $-0.06 \times (-8.91) = 0.5346 \text{ V}$

c. When 50 mL of 0.2 M NaOH (= $50 \times 0.2 = 10$ mmol = 10 mEq) is added to 100 mL of 0.05 M H_2SO_4 to the positive terminal of battery, then

mEq of NaOH = 10
mEq of
$$H_2SO_4 = 100 \text{ mL} \times 0.05 \times 2 \text{ (n factor)}$$

When 10 mEq of H_2SO_4 reacts with 10 mEq of NaOH, a salt (Na_2SO_4) of S_A/S_B is formed, which does not hydrolyze. So pH of such solution is = 7.

$$pH_c = 7$$
$$pH_c = ?$$

HA is a weak acid whose $pK_a = 7$ (determined in part (a) above) and $[HA] = 0.1 M = 10^{-1} M$.

Thus,
$$pH_{wA} = \frac{1}{2} (pK_a - \log C)$$

= $\frac{1}{2} (7 - \log 10^{-1}) = 4$

Hence,

$$E_{\text{cell}} = -0.06 \text{ (pH}_{\text{c}} - \text{pH}_{\text{a}})$$

= -0.06 (7 - 4) = -0.06 × 3 = -0.18 V

ILLUSTRATION 3.33

A hydrogen electrode placed in a solution containing CH_3COOK and CH_3COOH in the ratio of a:b and b:a has electrode potential values of -1.59 and +1.0 V, respectively. Calculate pK_a of CH_3COOH .

Sol. Mixture of CH₃COOK (salt of W_A/S_B) and CH₃COOH (W_A) forms acidic buffer solution whose pH is

$$pH_{acidic buffer} = pK_a + log \frac{[Salt]}{[Acid]}$$

$$\therefore E_{1(H_2)} = -0.059 \text{ pH}_1 = -0.059 \left[pK_a + log \frac{a}{b} \right] \qquad ...(i)$$

$$E_{2(H_2)} = -0.059 \text{ pH}_2 = -0.059 \left[pK_a + log \frac{b}{a} \right] \qquad ...(ii)$$

Adding Eqs. (i) and (ii), we get

$$E_1 + E_2 = -0.059 \left[pK_a + \log \frac{a}{b} \right] - 0.059 \left[pK_a + \log \frac{b}{a} \right]$$

$$= -2 \times 0.059 \ pK_a$$

$$\therefore pK_a = \frac{-(E_1 + E_2)}{2 \times 0.059} = \frac{-(-1.59 + 1.0)}{2 \times 0.059}$$

$$= \frac{0.59}{2 \times 0.059} = 5$$

$$\therefore pK_a = 5$$

ILLUSTRATION 3.34

Calculate the charge on mercurous ion and its magnetic moment. EMF of the cell given below is 0.0295 V at 25°C.

Sol. The given cell is an electrolytic concentration cell.

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{n_{\text{cell}}} \log \frac{[C]_{\text{anode}}}{[C]_{\text{cathode}}}$$
$$= 0 - \frac{0.059}{n_{\text{cell}}} \log \frac{0.01}{0.1}$$
$$n_{\text{cell}} = 0 - \frac{0.059}{0.0295} = 2$$

Thus, charge on mercurous ion (Hg_2^{2+}) is +2. Hg_2^{2+} exists as Hg^{\oplus} - Hg^{\oplus} and its magnetic moment is zero since there is no unpaired electron present in it.

3.10 VARIOUS TYPES OF HALF CELLS

a. Metal in contact with its ions

A metal (M) is contact with its ion (M^{n+}) is represented as M/ M^{n+} when it acts as oxidation electrode (anode) and M^{n+}/M when it acts as reduction electrode (cathode). Whether a given electrode acts as anode or cathode depends upon the other electrode with which it forms an electrochemical cell.

For example,

i. $Ag(s) \mid Ag^{\oplus}$ (aq), (acts as oxidation electrode)

(or)
$$Ag(s) \longrightarrow Ag^{\oplus} (aq) + e^{-}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - 0.059 \log \left[Ag^{\oplus} \right]$$

ii.
$$Ag^{\oplus}(aq) + e^- \longrightarrow Ag(s)$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - 0.059 \log \frac{1}{[\text{Ag}^{\oplus}]}$$

Note: Symbol "|" denotes the phase separation between the two electrodes.

b. Gaseous electrode

Gases such as H₂ and Cl₂ can act as anode and as cathode by loosing electrons and by accepting electrons, respectively. For example,

i. Pt, $H_2 \mid H^{\oplus}$ (acts as oxidation potential)

or
$$\frac{1}{2}$$
 H₂(g) (1 atm) \longrightarrow H ^{\oplus} (aq) + e⁻

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{1} \log \left[H^{\oplus} \right]$$

$$= 0 + 0.059 \text{ pH}$$

ii. $H^{\oplus} \mid H_2(g)$ (1 atm) (acts as reduction electrode)

$$\mathrm{H}^{\oplus}(\mathrm{aq}) + e^{-} \longrightarrow \frac{1}{2} \mathrm{H}_{2}(\mathrm{g}) (1 \mathrm{\ atm})$$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{1} \log \frac{1}{[H^{\oplus}]} = 0 - 0.059 \text{ pH}$$

iii.Pt, $\operatorname{Cl}_2(g)(1 \text{ atm}) | \operatorname{Cl}^{\odot}(aq)$, (acts as oxidation electrode)

$$Cl^{\odot}$$
 (aq) $\longrightarrow \frac{1}{2} Cl_2(g) (1 \text{ atm}) + e^-$

$$E_{\rm cell} = E^{\odot}_{\rm cell} - \frac{0.059}{1} \log \frac{1}{[{\rm Cl}^{\odot}]}$$

iv. Cl^{\odot} (aq) | $Cl_2(g)$ (1 atm), Pt (acts as reduction electrode)

$$e^- + \frac{1}{2} \operatorname{Cl}_2(g) (1 \text{ atm}) \longrightarrow \operatorname{Cl}^{\Theta} (aq)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{1} \log [\text{Cl}^{\odot}]$$

c. Calomel electrode

A calomel electrode consists of Hg covered with $\mathrm{Hg_2Cl_2}$ (mercurous chloride) (calomel) in contact with a solution of KCl (Fig. 3.6)

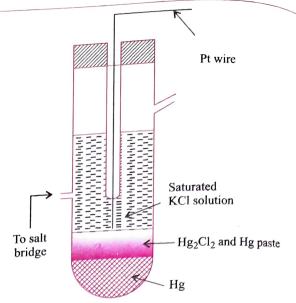


Fig. 3.6 Calomel electrode

Electrode representation: Hg(1), $Hg_2Cl_2(s) \mid Cl^{\odot}$ (aq) Anode reaction:

$$2\text{Hg(l)} + 2\text{Cl}^{\odot} \text{ (aq)} \Longrightarrow \text{Hg}_2\text{Cl}_2(\text{s}) + 2e^{-}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log \frac{1}{[\text{Cl}^{\odot}]^2}$$

Cathode reaction:

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^{\Theta}(aq)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log \left[\text{Cl}^{\odot} \right]^2$$

Three types of calomel electrodes generally used are:

i. Most common calomel electrode is the standard calomel electrode (SCE) in which the concentration of KCl is at its saturation (about 3.5 M).

 $E_{\rm SCE} \approx 0.24 \text{ V}$ (with respect to SHE)

- ii. Normal calomel electrode (NCE) in which 1.0 N KCl is used ($E_{NCE} = 0.268 \text{ V}$).
- iii. Decinormal calomel electrode in which 0.1 N KCl is used ($E_{\rm DNCE} = 0.338$ V). These electrodes are very handy and can be made easily.

d. Metal-insoluble salt anion electrode, e.g., Ag-AgCl electrode

It consists of a pure silver wire or sheet in a solution of K^{Cl} saturated with solid AgCl.

Electrode represented: Ag(s), AgCl | Cl[©](aq) (1 M) Cathode reaction:

$$AgCl(s) + e^{-} \Longrightarrow Ag(s) + Cl^{\Theta}(aq)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log[\text{Cl}^{\odot}] \qquad (E_{\text{reduction}}^{\odot} = 0.222 \text{ V})$$

Anode reaction:

$$Ag(s) + Cl^{\Theta}(aq) \iff AgCl(s) + e^{-}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{1} \log \frac{1}{[\text{Cl}^{\odot}]}$$

3.33

In saturated solution, $E^{\odot}_{\text{reduction}} = 0.197 \text{ V}$ (with respect to

Mercury-mercurous sulphate (Hg-Hg₂SO₄) electrode

Mercury-mercurous sulphate (Hg-Hg₂SO₄) elect

 $_{\text{Electrode}}^{\text{504}}$ representation: Hg(l), Hg₂SO₄ (s) | SO₄²⁻ (aq).

Cathode reaction:

Cathode reaction:

$$Hg_2SO_4(s) + 2e^- \longrightarrow 2Hg(l) + SO_4^{2-}$$
 (aq)

$$E_{\text{cell}} = E_{\text{cell}} - \frac{0.059}{2} \log [SO_4^{2-}]$$

$$E_{\text{reduction}}^{\circ} = 0.616 \text{ V (with respect to SHE)}$$

Anode reaction:

$$_{2\text{Hg(l)}} + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{Hg}_2\text{SO}_4(\text{s}) + 2\text{e}^{-}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log \frac{1}{[SO_4^{2-}]}$$

f. Mercury-mercuric sulphate (Hg-HgSO₄) electrode

It consists of Hg covered with sparingly soluble $HgSO_4$ in contact with H_2SO_4 or K_2SO_4 (Source of SO_4^{2-} ions). Electrode representation: Hg(1), $HgSO_4(s) | SO_4^{2-}(aq)$

Cathode reaction:

$$HgSO_4(s) + 2e^- \longrightarrow Hg(1) + SO_4^{2-}(aq)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log [SO_4^{2-}]$$

Anode reaction:

$$Hg(l) + SO_4^{2-}(aq) \longrightarrow Hg SO_4(s) + 2e^{-}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log \frac{1}{[SO_4^{2-}]}$$

Note: Ag-AgCl, Hg-Hg₂SO₄, Hg-HgSO₄, and calomel electrode are secondary reference electrodes.

g. Amalgam electrodes

It is a modified type of metal/metal-ion electrode in which metal sheet is replaced by metal amalgam, e.g.,

Na (in Hg at $c_1 M$) | Na \oplus ($c_2 M$) and

Cd (in Hg at c_1 M) | Cd²⁺ (c_2 M).

Cathode reaction:

$$e^- + Na^{\oplus} (C_2 M) \longrightarrow Na-Hg$$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{1} \log \frac{1}{[\text{Na}^{\oplus}]}$$

Anode reaction:

$$Na (in Hg) \longrightarrow Na^{\oplus} (C_2 M) + e^{-}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{1} \log [\text{Na}^{\oplus}]$$

The importance of these electrodes lies in the fact that active metals, such as Na and K which as such would react with water can be made reversible to their ions by dissolving them in mercury

h. Redox electrode

In this type, Pt wire is dipped in an electrolyte containing ions of an element in more than one oxidation state (e.g., Fe²⁺and Fe³⁺ ions). The electrode (inert material wire) acts as a source/sink for electrons.

Electrode representation: $Pt(s) \mid Fe^{2+}(aq), Fe^{3+}(aq)$

Cathode reaction:

$$Fe^{3+}$$
 (aq) + $e^- \longrightarrow Fe^{2+}$ (aq)

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

Anode reaction:

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^{-}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

i. Quinhydrone electrode

Redox electrodes can also be made by using substances that exists in two different oxidation states. Quinhydrone is an equimolar mixture of benzoquinone (Q) and hydroquinone (H_2Q) .

Electrode representation: Pt | Quinhydrone | $H^{\oplus}(aq)$ Cathode reaction:

or

$$Q(s) + 2H^{\oplus} + 2e^{-} \longrightarrow H_2Q(s)$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log \frac{1}{\left[\text{H}^{\oplus}\right]^2}$$

$$=E_{\text{cell}}^{\odot}-0.059 \text{ pH}$$

$$(E_{\text{reduction}}^{\odot} = 0.6994 \text{ V})$$

Anode representation:

$$OH \longrightarrow OH \longrightarrow OH + 2H^{\oplus} + 2e^{-1}$$

$$OH \longrightarrow OH$$

$$O$$
or

$$H_2Q(s) \longrightarrow Q(s) + 2H^{\oplus} + 2e^{-}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log [H^{\oplus}]^2$$

$$= E_{\text{cell}}^{\Theta} + 0.059 \text{ pH}$$

 The quinhydrone electrode is combined with a saturated calomel electrode to form a cell. It is represented as: Hg, Hg₂Cl₂(s), KCl (saturated solution) \parallel H $^{\oplus}$ (unknown ione) Q, QH₂ \mid Pt

$$\begin{split} E_{(\mathrm{Q,\,2H^{\bigoplus}\,|\,H_2Q})} &= E^{\ominus}_{(\mathrm{Q,\,2H^{\bigoplus}/H_2Q})} - 0.059 \text{ pH} \\ &= 0.6994 \text{ V} - 0.059 \text{ pH} \\ E_{\mathrm{SCE}} &= 0.24 \text{ V} \\ E_{\mathrm{cell}} &= E_{(\mathrm{Q,\,2H^{\bigoplus}\,|\,H_2Q})} - E_{\mathrm{SCE}} \\ E_{\mathrm{cell}} &= 0.699 \text{ V} - 0.059 \text{ pH} - 0.24 \text{ V} \\ \mathrm{pH} &= \frac{0.699 - 0.24 - E_{\mathrm{cell}}}{0.059} \end{split}$$

ii. Limitation of quinhydrone electrode: It cannot be used for solution of pH > 8. In more alkaline solutions, hydroquinone (H₂Q) ionizes appreciably as an acid and also gets oxidized partly by atmospheric oxygen. This alters the normal equilibrium between quinone and hydroquinone which forms the basis of a quinhydrone electrode.

j. Glass electrode

A glass electrode consists of a glass tube with thin-walled bulb A at the bottom (Fig. 3.7). For this purpose special glass having low melting point and high electrical conductivity is used. A solution of 0.1 M HCl, which furnishes a constant $[H^{\oplus}]$, is placed inside the bulb and an Ag, AgCl electrode or simply a Pt-wire is inserted to make electrical contact as shown. The reference electrode employed is usually the calomel electrode.

The functioning of this electrode depends on the potential difference across the glass membrane separating solutions of different pH. The electrode potential is given by the usual type or equation for a reversible hydrogen electrode, e.g.,

$$E_{\rm G} = E_{\rm G}^{\odot} - 0.059 \log \frac{1}{[{\rm H}^{\oplus}]}$$

= $E_{\rm G}^{\odot} - 0.059 \, {\rm pH}$

The cell representation is:

Pt, 0.1 M HCl | Glass | Experimental solution | KCl (salt solution), Hg₂Cl₂, Hg.

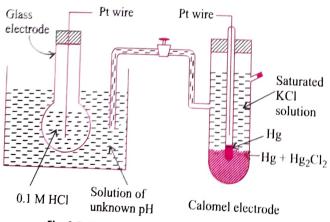


Fig. 3.7 Determination of pH by glass electrode

Since the potential of the calomel electrode is known, that of glass electrode can be easily calculated and the pH of the experimental solution is evaluated. The value of E^{\odot}_{G} is first obtained by working with solution of known pH.

$$\begin{split} E_G &= E^{\ominus}_G - 0.059 \text{ pH} \\ E_{\text{SCE}} &= 0.24 \text{ V} \\ E_{\text{cell}} &= E_{\text{SCE}} - E_G \\ &= 0.24 \text{ V} - (E^{\ominus}_G - 0.059 \text{ pH}) \\ &= 0.24 \text{ V} - E^{\ominus}_G + 0.059 \text{ pH} \\ &\therefore \text{ pH} = \frac{E_{\text{cell}} - 0.24 + E^{\ominus}_G}{0.059} \text{ at } 25^{\circ}\text{C} \end{split}$$

The advantages of glass electrode over other electrodes.

- i. It can be used even in strong oxidizing solutions which interfere even with quinhydrone electrode.
- ii. It can also be used in the presence of metallic long poisons, etc.
- iii. It is simple to operate and is, therefore, extensively used in chemicals, industrial, agricultural, and biological laboratories.

ILLUSTRATION 3.35

The quinhydrone electrode $(Q, H^{\oplus} | H_2 Q)$ is used in conjunction with a saturated calomel electrode, as represented below:

$$Hg(l),Hg_2Cl_2(s)$$
 | KCl (saturated | H^{\oplus} | (Unknown) | Q,H_2Q,P_1

 $EMF_{cell} = 0.264 \text{ V}$ at 30°C. Calculate the pH of unknown solution at this temperature.

Given:
$$E_{\text{calomel}} = 0.24 \text{ V}$$
 and $E_{2H^{\oplus}, Q|H_2Q}^{\ominus} = 0.7 \text{ V}$

Sol. (Note that the value
$$2.303 \frac{RT}{F}$$
 at $30^{\circ}\text{C} = 0.06$)

$$E_{\text{SCE}} = 0.24 \text{ V}$$

$$E_{\text{quinhydrone}} = E_{\text{quinhydrone}}^{\odot} - 0.06 \text{ pH (at 30°C)}$$

$$\therefore E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = E_{\text{quinhydrone}} - E_{\text{SCE}}$$

$$0.264 \text{ V} = 0.7 - 0.06 \text{ pH} - 0.24 \text{ (at 30°C)}$$

$$\therefore \text{pH} = \frac{0.7 - 0.24 - 0.264}{0.06} = 3.266 \approx 3.27$$

ILLUSTRATION 3.36

Glass electrode Buffer solution Standard calomel electrode

If the EMF of the above cell is 0.03 V, $E_{\text{SCE}} = 0.24 \text{ V}$, $E_{\text{SCE}} = 0.51 \text{ V}$, then calculate the pH of buffer solution at 30°C.

Sol.
$$E_{\text{glass}} = E_{\text{glass}}^{\Theta} - 0.06 \text{ pH (at } 30^{\circ}\text{C})$$

 $E_{\text{SCE}} = 0.24 \text{ V}$
 $\therefore E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}}$
 $= E_{\text{SCE}} - E_{\text{glass}}$
 $0.03 \text{ V} = 0.24 \text{ V} - (E_{\text{glass}}^{\Theta} - 0.06 \text{ pH) (at } 30^{\circ}\text{ C})$
 $\Rightarrow 0.03 \text{ V} = 0.24 \text{ V} - (0.51 - 0.06 \text{ pH)}$

$$E_{\text{cell}} = \frac{0.24 + E_{\text{glass}}^{\odot}}{0.06}$$

$$= \frac{0.03 - 0.24 + 0.51}{0.06} = 5$$

11 RELATION BETWEEN EMF, SOLUBILITY, AND SOLUBILITY PRODUCT OF A SPARINGLY SOLUBLE SALT

The solubility product of a sparingly soluble salt is a kind of equilibrium constant. Consider the salt AgX in equilibrium with its ions in a saturated solution.

$$AgX(s) \Longrightarrow Ag^{\oplus}(aq) + X^{\ominus}(aq)$$

 $K_{\text{sp}} = a_{\text{Ag}} \oplus \times a_{\text{X}} \ominus = [\text{Ag}^{\oplus}] [\text{X}^{\ominus}]$, assuming an ideal solution so that activities (a) equal concentrations. The above reaction is the cell reaction for the following cell:

 $_{\mathbb{A}^{\underline{G}}}|\mathbb{A}^{\oplus}X^{\ominus}$ (saturated solution) $\|\mathbb{A}gX(c)\|\mathbb{A}g$

The half cell reactions are:

$$Ag \iff Ag^{\oplus}(aq) + e^{-}$$

$$Ag^{\oplus}X^{\ominus}(c) + e^{-} \rightleftharpoons Ag + X^{\ominus}$$

$$Ag^{\oplus}(c) \rightleftharpoons Ag^{\oplus}(unknown) + X^{\ominus}(aq)$$

This is a type electrolytic concentration cell is which $E_{cell}^{\odot} = 0.0 \text{ V}$.

$$\therefore E_{\text{cell}} = E^{\ominus}_{\text{Cell}} - \frac{0.059}{n_{\text{cell}}} \log \frac{[\text{Ag}^{\oplus}] (\text{unknown})}{[\text{Ag}^{\oplus}] (\text{known conc. } c)}$$

$$=0-\frac{0.059}{1}\log\frac{[\mathrm{Ag}^{\oplus}]}{c}$$

Hence, [Ag[⊕]] in LHS is evaluated.

Thus,
$$K_{\rm sp} = [Ag^{\oplus}][X^{\ominus}] = [Ag^{\oplus}]^2$$

and solubility (S) =
$$\sqrt{K_{\rm sp}}$$

b. If E^{\odot} of X^{\odot} | AgX, Ag half cell is given, then $K_{\rm sp}$ of AgX can be calculated by using equation:

$$Ag(s) \rightleftharpoons Ag^{\oplus}(aq) + e^{-s}$$

Cathode reaction:
$$Ag^{\oplus}(s) + e^{-} \rightleftharpoons Ag(s) + X^{\ominus}(s)$$

Cell reaction:

$$AgX(s) \rightleftharpoons Ag^{\oplus}(aq) + X^{\ominus}(aq)$$

$$\begin{aligned} E_{\text{cell}} &= (E^{\odot}_{\text{reduction}})_{\text{c}} - (E^{\odot}_{\text{reduction}})_{\text{a}} \\ &= E^{\odot}_{\text{AgX, Ag} \mid X^{\odot}} - E^{\odot}_{\text{Ag}^{\oplus} \mid \text{Ag}} \end{aligned}$$

Since at equilibrium, $E_{\text{cell}} = 0$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{1} \log \left[Ag^{\oplus} \right] \left[X^{\odot} \right]$$

$$0 = E^{\odot}_{\text{cell}} - 0.059 \log K_{\text{sp}}$$

$$\therefore E^{\odot}_{\text{cell}} = 0.059 \log K_{\text{sp}} \qquad ...(i)$$

Thus, knowing E_{cell}^{\odot} , the K_{sp} of a sparingly soluble salt can be calculated. Equation (i) is used when the half cell contains electrolyte in saturated solution.

ILLUSTRATION 3.37

For galvanic cell,

Ag | AgCl (s), CsCl (0.1 M) || Cs Br (10⁻³ M), AgBr (s) | Ag.

Calculate the EMF generated and assign correct polarity to each electrode for spontaneous or exergonic process at 25°C.

Given:
$$K_{sp}$$
 of AgCl = 3.0 × 10⁻¹⁰; K_{sp} of AgBr = 4.0 × 10⁻¹³.

Sol. LHS electrode

$$K_{\rm sp} = [Ag^{\oplus}][Cl^{\ominus}] = [Ag^{\oplus}]_a(0.1)$$

$$3.0 \times 10^{-10} = [Ag^{\oplus}]_a(0.1)$$

$$\therefore [Ag^{\oplus}]_a = \frac{3.0 \times 10^{-10}}{0.1 \text{ M}} = 3.0 \times 10^{-9} \text{ M}$$

RHS electrode:

$$K_{\rm sp} = [{\rm Ag}^{\oplus}]_{\rm c} [{\rm Br}^{\ominus}]$$

$$4.0 \times 10^{-13} = [Ag^{\oplus}]_c (10^{-3} \text{ M})$$

It is a concentration cell, $:: E^{\ominus}_{cell} = 0.$

Half cell reactions are

Anode reaction:

$$Ag(s) \rightleftharpoons Ag^{\oplus}(aq) + e^{-}$$

Cathode reaction: $Ag^{\oplus}(cathode) + e^{-} \iff Ag(s)$

Cell reaction:

$$Ag^{\oplus}(cathode) \iff Ag^{\oplus}(anode)$$

Thus,

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.059}{1} \log \frac{[Ag^{\oplus}]_a}{[Ag^{\oplus}]_c}$$

$$= 0 - \frac{0.059}{1} \log \frac{3.0 \times 10^{-9}}{4 \times 10^{-10}} \qquad \text{(Take } 0.059 \approx 0.06)$$

$$= -0.06 [\log 30 - 2 \log 2]$$

$$= -0.06 [1.48 - 2 \times 0.3]$$

$$= -0.0528 \text{ V}$$

 $E_{\rm cell} = -{\rm ve}$, suggest that cell is non-spontaneous or endergonic ($\Delta G = +{\rm ve}$). For spontaneous process, the polarity of electrodes has to be reversed, i.e., change anode to cathode and cathode to anode.

ILLUSTRATION 3.38

EMF of the cell

 $Ag|AgNO_3(0.1 \text{ M}) \parallel K Br(1 \text{ N}), AgBr(s)|Ag \text{ is } -0.6 \text{ V} \text{ at } 298 \text{ K}$ $AgNO_3$ is 80% and KBr is 60% dissociated.

Calculate a. Solubility and

b.
$$K_{\rm sp}$$
 of AgBr at 298 K.

Sol. The above cell is a concentration cell.

$$\therefore E^{\odot}_{\text{cell}} = 0.0 \text{ V}$$

The half cell reactions are

Anode reaction: Ag(anode) \iff Ag $^{\oplus}$ (0.1 M) + c Cathode reaction:

$$Ag^{\oplus}(cathode) + e^{-} \Longrightarrow Ags(cathode)$$

Cell reaction: Ag[⊕](cathode) ===== Ag[⊕](0.1 M)_{anode}

Since AgNO3 is 80% ionized.

$$[Ag^{\oplus}]_a = 0.1 \times \frac{80}{100} = 0.08 \text{ M}$$

$$\therefore E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.06}{1} \log \frac{[Ag^{\oplus}]_a}{[Ag^{\oplus}]_c} \quad \text{(Take 0.059 \pi 0.06)}$$

$$-0.6 \text{ V} = 0 - 0.06 \log \frac{0.08}{[Ag^{\oplus}]_c}$$

$$\log \left[Ag^{\oplus} \right]_{c} = \log 0.08 - 10 = (\log 2^{3} - \log 100) - 10$$
$$= 0.9 - 2 - 10 = -11.1$$

:.
$$[Ag^{\oplus}]_c = Antilog(-11.1) = Antilog(\overline{12.9}) = 7.9 \times 10^{-12}$$

 $\approx 8 \times 10^{-12} M$

Since KBr is 60% dissociated,

$$[Br^{\odot}] = 1 \times \frac{60}{100} = 0.6 \text{ M}$$

$$K_{sp} = [Ag^{\oplus}] [Br^{\odot}] = 8 \times 10^{-12} \times 0.6 = 4.8 \times 10^{-12} M^2$$
Solubility (S) = $\sqrt{K_{sp}} = \sqrt{4.8 \times 10^{-6}} M$

$$= 2.19 \times 10^{-6} M$$

ILLUSTRATION 3.39

Estimate the E^{\odot} reduction for Cu | CuS electrode.

Given:
$$K_{\rm sp}$$
 of CuS = 8.0×10^{-36} ; $E^{\odot}_{\rm (Cu \mid cu^{2+})} = -0.34 \text{ V}$

Sol. Half cell reactions are

Anode reaction:

$$\mathcal{L}_{\mathsf{u}} \Longrightarrow \mathsf{C}\mathsf{u}^{2^+} + \mathcal{L}_{\mathsf{u}}$$

Cathode reaction: $CuS + 2e \iff Cu + S^{2-}$

Cell reaction:

$$CuS \rightleftharpoons Cu^{2+} + S^{2-}$$

$$E^{\odot}_{cell} = (E^{\odot}_{reduction})_c - (E^{\odot}_{reduction})_a$$

$$= E^{\odot}_{(Cus \mid Cu)} - E^{\odot}_{(Cu^{2+} \mid Cu)}$$

$$= x - 0.34 \text{ V}$$

Cell is in equilibrium, therefore, $E_{cell} = 0$.

:
$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log [\text{Cu}^{2+}][\text{S}^2]$$

$$0 = (x - 0.34\text{V}) - \frac{0.06}{2} \log K_{sp} \qquad \text{(Take } 0.059 \approx 0.06\text{)}$$

$$\therefore E^{\odot}_{\text{cell}} = \frac{0.06}{2} \log K_{\text{sp}} = 0.03 \log (8 \times 10^{-36})$$
$$= 0.03 [3 \log 2 - 36] = 0.03 [3 \times 0.3 - 36]$$

$$= 0.03 \times -35.1 = -1.053 \text{ V} \approx 1.05 \text{ V}$$

$$(x - 0.34) = -1.05 \text{ V}$$

$$r = -0.71 \text{ V}$$

 $E^{\odot}_{\text{(CuS | Cu)}}$ (standard reduction potential) = -0.71 V

CONCEPT APPLICATION EXERCISE 3,1

1. 500 L of a solution 0.1 M in [Au(CN)₂][©] and 0.003 M is [Ag(CN)₂][©] was evapourated to one-third of original volume and was treated with zinc (40 g). Assuming that all these redox reactions undergo essentially to completion, calculate the concentration of [Au(CN)₂][©] and [Ag(CN)₂]^E after reaction has ceased.

Given:

a.
$$[Zn(CN)_4]^{2^-} + 2e^- \longrightarrow Zn + 4CN^{\odot} \mid E^{\odot} = -1.260$$

b.
$$[Au(CN)_2]^{\odot} + e^- \longrightarrow Au + 2CN^{\odot}$$
 $E^{\odot} = -0.6 \text{ V}$

c.
$$[Ag(CN)_2]^{\ominus} + e^- \longrightarrow Ag + 2CN^{\ominus}$$
 $E^{\ominus} = -0.31\text{ W}$

2. A silver electrode is immersed in saturated Ag_2SO_4 (aq). The potential difference between Ag and SHE is found to be 0.70 at 25°C. Determine $K_{\rm sp}$ of Ag_2SO_4 solution.

Given: $E^{\odot}_{Ag}^{\oplus}|_{Ag} = 0.79 \text{ V}.$

3. Calculate the reduction potential of an electrode which was originally 0.1 M $\rm MnO_4^{\, \odot}$ and 0.5 M $\rm H^{\oplus}$ and has been treated with 50% of Fe²⁺ ions required to reduce all $\rm MnO_4^{\, \odot}$ to $\rm Mn^{2+}$.

Given: $E^{\odot}_{MnO_4}^{\odot}|_{Mn^{2+}} = 1.50 \text{ V}$

4. Two Daniell cells contain the same solution of ZnSO₄ but differ in the CuSO₄ solution. The EMF of the cell containing 0.5 M CuSO₄ is higher than the other cell by 0.06 V. Calculate the concentration of CuSO₄ in the other cell.

$$\left(\text{Take } \frac{2.303 \ RT}{F} \approx 0.06\right)$$

5. Calculate the degree of hydrolysis (h) and hydrolysis

constant of anilinium hydrochloride (Ph NH₃Cl²) in M/30 solution of salt at 298 K from the following cell data:

Pt, H₂(1 atm) | H^{\oplus}(1M) || Ph NH₃Cl^{\ominus} (M/30) | H₂(1 am), Pt. $E_{\text{cell}} = -0.1777 \text{ V}.$

6. The half cell potential of a half cell A^{x+} , $A^{(x+n)^+} \mid Pt^{-is}$ found to be as follows:

a. Percent of reducing form

25

b. Cell potential/V

0.10 0.115

0.10

Determine the value of n.

ANSWERS

1. 0.0018 M

2. $1.35 \times 10^{-5} \text{ M}^2$

3. 1.40 V

50

4. $5 \times 10^{-3} \text{ M}$

5. h = 0.03; $K_h = 3.33 \times 10^{-5}$

6. 2

12 ELECTROLYSIS which an electric current causes a chemical change to chemical energy is column of electric energy to chemical energy is column. Process in which are mainly two ways in which are there are mainly two ways in which are the true to the mainly two ways in which are the true to the or called as mainly two ways in which analysis is done mainly two ways in which analysis is done

Qualitative electrolysis: Study of possible products formed thode and anode. electrolysis: at cathode and anode.

Quantitative electrolysis: Study of amount/moles/volume Quantitative of the products formed at cathode and anode during electrolysis.

312.1 QUALITATIVE ELECTROLYSIS

Rectrolysis of Molten Salts of Some Compounds

Molten NaCl (an electrolyte) means free sodium ions (Na[®] ions) and chloride ions (Cl[©] ions) so it conducts current with the help of ions. As electric current is passed in the cell, Cl[©] ions are attracted to anode (+ve electrode) and Na[®] ions to cathode (-ve electrode). Both ions are discharged at respective electrode as follows (Fig. 3.8)

$$2Cl^{\ominus} \longrightarrow Cl_2(g) + 2e^-$$
 [Oxidation]

Cathode:
$$Na^{\oplus} + e^{-} \longrightarrow Na(s)$$

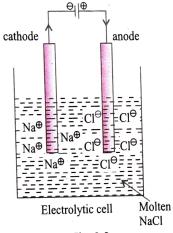
Overall reaction:
$$2Na^{\oplus} + 2Cl^{\ominus} \longrightarrow 2Na(s) + Cl_{2}(g)$$

This type of cell is also called as electrolytic cell. The

basic difference between an electrolytic cell and a galvanic (or voltaic) cell is that a galvanic cell produces electricity whereas an electrolytic cell consumes electricity.

The importance of electrolytic cell is that it is widely used in isolation and purification of various elements and gases.

Products of electrolysis depend mainly on the following factors:



- Fig. 3.8
- i. Electrode potential of various possible reactions (deposition or liberation) at cathode or anode.
- ii. Over potential of gases w.r.t. the electrode (material) at which they are liberating.
- iii. Concentration of the ions (to be oxidized or reduced) in the solution.
- iv. Type of electrodes [reacting or non-reacting {e.g., Pt, C (graphite)}].
- b. Electrolysis of molten chlorides of potassium and magnesium produces K and Mg metals at cathode and Cl₂(g) at anode, when dc voltage is applied to the two electrodes. Similarly, Al metal is produced at cathode by

the electrolysis of molten aluminium oxide (Al₂O₃) in the presence of cryolite (Na₃AlF₆) and fluorspar (CaF₂) using carbon electrodes. The oxygen liberated at the anode reacts with C-anode producing CO and CO₂. The overall reactions of some molten or fused compounds may be written as:

$$[KCl \longrightarrow K^{\oplus} + Cl^{\ominus}]$$

$$2Cl^{\odot} \longrightarrow Cl_2(g) + 2e^{-g}$$

$$2K^{\oplus} + 2e^{-} \longrightarrow 2K(s)$$

Overall reaction:
$$2K^{\oplus} + 2Cl^{\ominus} \longrightarrow 2K(s) + Cl_2(g)$$

Molten $MgCl_2$: $[MgCl_2 \longrightarrow Mg^{2+} + 2Cl^{\ominus}]$

$$MgCl_2 \longrightarrow Mg + 2Cl - 1$$

$$2Cl^{\odot} \longrightarrow Cl_{2}(g) + 2e^{-}[Oxidation]$$

$$Mg^{+2} + 2e^{-} \longrightarrow Mg(s) [Reduction]$$

Overall reaction:

$$\frac{Mg^{+2} + 2Cl^{\odot} \longrightarrow Mg(s) + Cl_2(g)}{Mg^{+2} + 2Cl^{\odot} \longrightarrow Mg(s) + Cl_2(g)}$$

$$[Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}]$$

$$\begin{bmatrix} C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^{-} \\ C(s) + 2O^{2-}(melt) \longrightarrow CO_{2}(g) + 4e^{-} \end{bmatrix}$$

[Oxidation]

$$2Al^{3+}$$
(melt) + $6e^{-} \longrightarrow 2Al(s)$ [Reduction]

Overall reaction:
$$2A1^{3+} + 3O^{2-} + 2C \longrightarrow CO_2 + CO + 2Al(s)$$

d. Molten K_2SO_4 : [$K_2SO_4 \longrightarrow 2K^{\oplus} + SO_4^{2-}$]

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$$
 [Oxidation]
 $\left(\begin{array}{c} Peroxodisulphate \\ ion \end{array}\right)$

Cathode:
$$2K^{\oplus} + 2e^{-} \rightarrow 2K$$
 [Reduction]

Overall
$$2K^{\oplus} + 2SO_4^{2-} \rightarrow 2K + S_2O_8^{2-}$$
 reaction:

e. Molten Na₂S₂O₃ (sodium thiosulphate):

$$[\mathrm{Na}_2\mathrm{S}_2\mathrm{O}_3 \to 2\mathrm{Na}^{\oplus} + \mathrm{S}_2\mathrm{O}_3^{2-}]$$

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$
 [Oxidation]

Cathode:

$$2Na^{\oplus} + 2e^{-} \rightarrow 2Na(s)$$
 [Reduction]

Overall
$$2Na^{\oplus} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2Na(s)$$

reaction:

Electrolysis of Aqueous Solutions of Some Compounds

Products of electrolysis depends on the nature of material being electrolyzed and the type of electrodes being used. If the electrode is inert (e.g., Pt or Au) it does not participate in the chemical reaction and acts only as source or sink for electrons. If the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes. The products of electrolysis depend on different oxidizing and reducing species present in the electrolytic cell and their standard electrode potentials. Some of the electrochemical processes, although feasible, are so slow kinetically that at lower voltages, these do not seem to take place

and extra potential (called over potential) has to be applied, which makes such process more difficult to occur.

Given below are some examples that include reactions each with a "x" mark (meaning the following oxidation/reduction will not take place) and a "\square" mark (meaning the oxidation/reduction will take place).

a. Electrolysis of aqueous NaCl solution (using inert electrode)

Note: When electrode is not mentioned, assume it to be Pt.

In aqueous solution of NaCl, Na[⊕], Cl[⊙], H[⊕](from water) and OH (from water) ions are free to move for the conduction of the electric current. When electric current is passed, Na[®] and H^{\oplus} ions are attracted to cathode and Cl^{Θ} and $\overset{\hookrightarrow}{OH}$ ions attracted to anode. The solution now contains four ions Na[⊕], Cl[©](from NaCl), H[⊕], OH (from water) and there is race amongst them for their discharge at their respective electrodes.

The following electrode reactions are possible:

Cathode:

*Na
$$\oplus$$
(aq) + $e^- \longrightarrow$ Na(s) $E_{\text{Na}} \oplus_{|\text{Na}} = -2.71 \text{V}$
 \checkmark 2H₂O(l) +2 $e^- \longrightarrow$ H₂(g) + 2 OH (aq)

 $E_{\text{H}_2\text{O} \mid \text{H}_2}^{\Theta} = -0.83\text{V}$

Anode:

$$\checkmark$$
2Cl $^{\odot}$ (aq) \longrightarrow Cl₂(g) + 2e⁻ $E^{\odot}_{\text{Cl}^{\odot} \mid \text{Cl}_{2}} = -1.36\text{V}$

 $\times 2H_2O(1) \longrightarrow O_2(g) + 4H^{\oplus}(aq) + 4e^{-1}$

$$E_{\text{H}_2\text{O} \mid \text{O}_2}^{\ominus} = -1.23\text{V}$$

Overall reaction: $2Na^{\oplus}(aq) + 2Cl^{\ominus}(aq) \longrightarrow Na(s) + Cl_{2}(g)$

In this electrolysis, H2 at cathode and Cl2 at anode are given off. Why Na[®] ions and OH ions are not discharged? The reason lies in the reduction potential values. Clearly, $E^{\ominus}_{Na} \oplus_{|Na} < E^{\ominus}_{H_2O|H_2}$

- i. Although Cl^o has lesser tendency to discharge (oxidize) [Cl[©]will be at anode where oxidation takes place] as compared to $\stackrel{\circleddash}{OH}$ (Cl $^{\boxdot}$ lies below $\stackrel{\boxdot}{OH}$ in the electrochemical series) at anode still OH will not be discharged (oxidize) due to concept of overpotential (Extra potential required to initiate a reaction at a required rate). Formation of O2 from H2O is kinetically very slow (i.e., low rate). Thus, OH ions will remain in the solution.
- ii. The aqueous solution of NaCl will become alkaline (due to the presence of OH ions) after electrolysis.
- iii. In the case of electrolysis of NaX(aq) (where $X^{\scriptscriptstyle \bigcirc}$ is Br $^{\odot}$, I $^{\odot}$), X $_2$ will be liberated at anode. Using NaF, O $_2$ gas will be liberated at anode instead. Also, $E^{\odot}_{Br^{\odot} \mid Br_{2}}$ = $-1.09 \,\text{V}$ and $E_{I_{\odot}|I_{2}}^{\odot} = -0.54 \,\text{V}$.

b. Aqueous CuSO₄ solution (using inert electrode) Possible reaction at:

Cathode:

✓
$$Cu^{2+}(aq) + 2e^{-}$$
 ← $Cu(s)$ $E^{\odot}_{Cu^{2+}|Cu} = +0.34 \text{ V}$

*
$$2H_2O(1) + 2e^- \longrightarrow H_2(g) + 2 \overset{\bigcirc}{OH} (aq)$$
 $E^{\ominus}_{H_2O|_{H_2}} = -0.83\sqrt{1}$

Anode:

* $2H_2O(1) \longrightarrow O_2(g) + 4H^+(aq) + 4e^ E^{\ominus}_{H_2O|_{O_2}} = -1.23\sqrt{1}$

* $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^ E^{\ominus}_{SO_4^{2-}|S_2O_8^{2-}} = -2.0\sqrt{1}$

Overall reaction:

$$2H_2O(1) + 2Cu^{2+}(aq) \longrightarrow 2Cu(s) + O_2(g) + 4H^{\oplus}(aq)$$

In this electrolysis, Cu at cathode and O₂ at anode and produced. Also, the aqueous solution of CuSO₄ will become acidic (due to the presence of H[⊕] ions) after electrolysis

c. Aqueous Na₂SO₄ solution (using inert electrode)

Possible reaction at:

Cathode:

× Na[⊕](aq) +
$$e^-$$
 → Na(s) $E_{\text{Na}}^{\ominus} = -2.7 \text{ y}$

✓ 2H₂O(l) +2 e^- → H₂(g) + 2 OH (aq)
$$E_{\text{H2O | H2}}^{\ominus} = -0.83 \text{ y}$$

Anode:

Anode:

$$\star 2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$$

 $E^{\oplus}_{SO_4^{2-}|S_2O_8^{2-}} = -2.01$
 $\star 2H_2O(1) \longrightarrow O_2(g) + 4H^{\oplus}(aq)$
 $E^{\oplus}_{H_2O|O_2} = -1.23$

Clearly, at cathode, Na[⊕](aq) ions will not be deposited the to their lower reduction potential than H₂O.

Similarly, SO₄²⁻ will not be oxidized due to their lower oxidation potential than H₂O.

Thus, the electrolysis of Na₂SO₄/K₂SO₄/CaSO₄/MgSO₄ Li₂SO₄ etc., is actually equivalent to electrolysis of H.O.

d. Aqueous NaCl solution (very dilute using inert electrode) Possible reactions at:

Cathode:

× Na[⊕](aq) +
$$e^-$$
 → Na(s) $E_{\text{Na}}^{\ominus}|_{\text{Na}} = -2.71 \text{ V}$
✓ 2H₂O(1) +2 e^- → H₂(g) + 2 OH (aq)
 $E_{\text{H2O}|_{\text{H2}}}^{\ominus} = -0.83$

Anode:

× 2Cl[©](aq) → Cl₂(g) + 2e⁻
$$E^{\odot}_{\text{Cl}^{\odot} \mid \text{Cl}_{2}} = -1.36 \text{ V}$$

∨ 2H₂O(l) → O₂(g) + 4H[⊕](aq) + 4e⁻ $E^{\odot}_{\text{H}_{2}O \mid \text{O}_{2}} = -1.23 \text{ V}$
When NaCl is highly dilute, there is a very less chance of Cl[©](due to their less availability) getting oxidized. So instead H₂O will get oxidized.

Note:
$$2\text{Cl}^{\ominus}(\text{aq}) \longrightarrow \text{Cl}_2(\text{g}) + 2e^{-}$$

$$E_{\text{Cl}^{\ominus}|\text{Cl}_2} = E^{\ominus}_{\text{Cl}^{\ominus}|\text{Cl}_2} - \frac{0.059}{2} \log \frac{p_{\text{Cl}_2}}{\left[\text{Cl}^{\ominus}\right]^2}$$

$$= E^{\ominus}_{\text{Cl}^{\ominus}|\text{Cl}_2} - \frac{0.059}{2} \log p_{\text{Cl}_2} + 0.059 \log \left[\text{Cl}^{\ominus}\right]$$
Thus, $E^{\ominus}_{\text{Cl}^{\ominus}|\text{Cl}_2}$ decreases as $\left[\text{Cl}^{\ominus}\right]$ decreases making the oxidation of H_2O more favourable.

NaCl solution (using Hg electrodes) (active in the land of the lan

electrode)

Possible reactions at:

possible reactions at:

$$C_{alho}de: \longrightarrow Na(s)$$
 $C_{alho}de: \longrightarrow Na(s)$
 $C_{alho}de: \longrightarrow Na(s$

$$\sqrt{Na^{\theta}(aq) + e} \longrightarrow H_2(g) + 2 \text{ OH (ac)}$$

$$E_{\rm H_2O \,|\, H_2}^{\odot} = -0.83 \,\rm V$$

$$E^{\odot}_{\text{Cl}^{\odot} \mid \text{Cl}_2} = -1.36 \text{ V}$$

$$E_{\text{H}_2\text{O} \mid \text{O}_2}^{\ominus} = -1.23 \text{ V}$$

When Hg electrodes are used instead of Pt, Na[®](aq) gets which further reacts with Hg to form sodium

$$\underset{\text{Na(s)} + \text{Hg(s)}}{\text{amalgam.}} \longrightarrow \text{NaHg(s)}$$

Aqueous CuSo₄ solution (using Cu electrodes) (active

Possible reactions at:

Cathode:

Cannote:

$$\sqrt{\text{Cu}^{2^{+}}(\text{aq})} + 2e^{-} \longrightarrow \text{Cu(s)} \ E^{\odot}_{\text{Cu}^{2^{+}} \mid \text{Cu}} = 0.34 \text{ V}$$

$$*2H_2O(1) + 2e^- \longrightarrow H_2(g) + 2OH (aq)$$

$$E^{\odot}_{\text{H}_2\text{O} \mid \text{H}_2} = -0.83 \text{ V}$$

$$*2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^{-}$$

$$E^{\odot}_{SO_4^{2-}|S_2O_8^{2-}} = -2.01 \text{ V}$$

$$E_{\text{H}_2\text{O} \mid \text{O}_2}^{\ominus} = -1.23 \text{ V}$$

$$\checkmark$$
Cu(s) \longrightarrow Cu²⁺(aq) + 2e⁻ $E^{\ominus}_{\text{Cu} \mid \text{Cu}^{2+}} = -0.34 \text{ V}$

$$\Theta_{\text{Cu}+\text{Cu}^2+} = -0.34 \text{ V}$$

Thus, when Cu is electrolyzed using Cu electrodes, Cu is dissolved (at Cu anode) and Cu is deposited (at Cu cathode).

Note: a. [Cu²⁺] in solution remain constant during electrolysis.

b. This technique is used in the refining of Cu. The impure Cu (95%) is made anode and thin a sheet of pure Cu is made cathode, and electrolysis is carried out to get pure Cu. The electrolyte is CuSO₄ solution acidified with dilute H2SO4. Impurities fall down as anode mud.

g. Aqueous AgNO3 solution (using Ag electrodes) (active electrode)

Possible reactions at:

Cathode:

$$\checkmark Ag^{\oplus}(aq) + e^{-} \longrightarrow Ag(s)$$

$$E_{Ag}^{\oplus}|_{Ag} = 0.8 \text{ V}$$

*2H₂O(l) +2e⁻
$$\longrightarrow$$
 H₂(g) + 2 OH (aq)
$$E^{\Theta}_{H_2O \mid H_2} = -0.83 \text{ V}$$
Anode.

$$E_{\text{H,O}+\text{H}_2} = -0.83 \text{ V}$$

Anode:

*2H₂O(l)
$$\rightarrow$$
 O₂(g) + 4H ^{\oplus} (aq) + 4e⁻ $E^{\ominus}_{\text{H}_2\text{O} \mid \text{O}_2} = -1.23 \text{ V}$

* $NO_3^{\odot}(aq) \rightarrow (No reaction)$

$$^{\vee}$$
 Ag(s) \rightarrow Ag $^{\oplus}$ (aq) + e

$$E_{\Delta_q \oplus_{\Delta_q} = -0.8}^{\Theta}$$

Thus, when aqueous AgNO₃ is electrolyzed using Ag electrodes, Ag is discalar. electrodes, Ag is dissolved at anode and deposited at cathode. [Ag[®]] in the solution remains constant during electrolysis. This method is used for the refining of Ag. Impure Ag (95%) is made anode and thin sheet of pure Ag is made cathode in AgNO₃ solution and electrolysis is carried out to get pure Ag. Impurities falls down as anode mud.

h. Aqueous H₂SO₄ solution (using inert electrode)

Possible reactions at:

Cathode:

Cathode:

$$\checkmark 2H_2O(1) + 2e^- \longrightarrow H_2(g) + 2 \stackrel{\odot}{OH} (aq)$$

 $E^{\odot}_{H_2O \mid H_2} = -0.83 \text{ V} \quad ...(i)$

*
$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^{-}$$

$$E^{\odot}_{SO_4^{2-}|S_2O_8^{2-}} = -1.96 \text{ V} \quad ...(ii)$$

$$2H_2O(1) \longrightarrow O_2(g) + 4H^{\oplus}(aq) + 4e^-$$

$$E^{\ominus}_{H_2O \mid O_2} = -1.23V \quad ...(iii)$$

$$E_{\text{H}_2\text{O}|\text{O}_2} = -1.23 \text{ V} \dots \text{(III)}$$

Note: For dilute H₂SO₄, reaction (iii) is preferred but at higher concentration of H₂SO₄ and high current density, reaction (ii) is preferred. When 50% aqueous solution of H2SO4 is used both reactions (ii) and (iii) occur simultaneously at anode.

i. Aqueous NiSO₄ solution (using inert electrode):

Possible reactions at:

Cathode:

$$\checkmark$$
 Ni²⁺(aq) +2e⁻ → Ni(s) $E^{\ominus}_{Ni}^{2+}/Ni} = -0.25 \text{ V}$

$$\star 2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH (aq)$$

$$E_{\text{H}_2\text{O} \mid \text{H}_2}^{\ominus} = -0.83\text{V}$$

Anode:

$$E^{\odot}_{SO_4}^{2-}/S_2^{O_8}^{2-} = -2.01 \text{ V}$$

$$\checkmark$$
 2H₂O(l) \longrightarrow O₂(g) + 4H ^{\oplus} (aq) + 4e⁻

$$E^{\Theta}_{\text{H}_2\text{O} \mid \text{O}_2} = -1.23 \text{ V}$$

Note: In practice, it has been observed that H, gas also gets liberated at cathode along with Ni.

j. Aqueous HCOONa (Kolbe's electrolysis)(using inert electrodes)

Possible reactions at:

Cathode:

$$\mathbf{x} \operatorname{Na}^{\oplus}(\operatorname{aq}) + e^{-} \longrightarrow \operatorname{Na}(\operatorname{s}) \quad E^{\ominus}_{\operatorname{Na}^{\oplus} \mid \operatorname{Na}} = -2.71 \operatorname{V}$$

$$\checkmark$$
 2H₂O(l) +2 $e^ \longrightarrow$ 2 OH (aq) + H₂(g)

$$E^{\odot}_{\rm H,O\,|\,H_2} = -0.83 \text{ V}$$

Anode:

$$2\text{HCOO}^{\Theta}(\text{aq}) \longrightarrow 2\text{HCOO}^{\bullet} + 2e^{-}$$

$$\downarrow^{-2\text{CO}_2}$$

$$H_2(g) \leftarrow 2H' + 2CO_2$$
 (g)

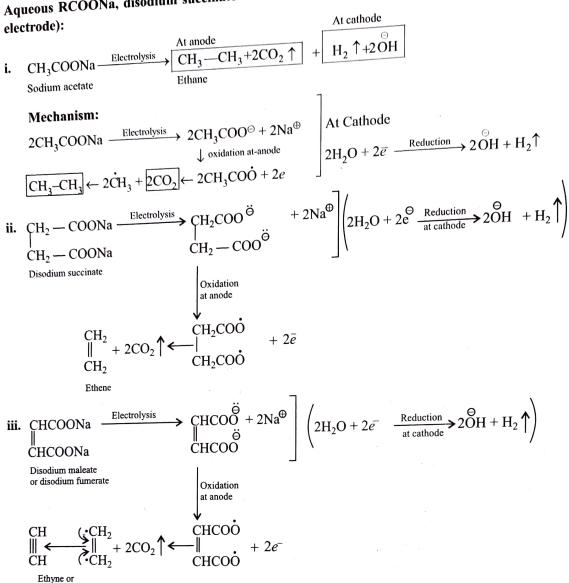
$$\checkmark$$
 2HCOO $^{\odot}$ (aq) \longrightarrow H₂(g) + 2CO₂(g) + 2 e^{-}

$$\times 2H_2O(1) \longrightarrow O_2(g) + 4H^{\oplus}(aq) + 4e^{-1}$$

$$E_{\text{H}_2\text{O} \mid \text{O}_2}^{\odot} = -1.23 \text{ V}$$

So in the electrolysis of aqueous solution of alkali metal salts (except Li) of HCOOH, using Pt electrode, H2(g) is liberated at cathode and H₂(g) and CO₂(g) are liberated at anode and the solution is basic (due to the presence of OH ions) after electrolysis.

8.40 Physical Chemistry k. Aqueous RCOONa, disodium succinate and disodium maleate or disodium fumerate (Kolbe's electrolytic) (using inert



L. General rules of electrolysis of aqueous solutions using inert electrode (✓ indicates that the oxidation/reduction will occur and * indicates that the oxidation/reduction will not occur)

acetylene

- i. (✓) Reduction potential of H₂O > (x) Reduction potential of cations of 1, 2, and 13 groups of periodic table, e.g., Na[⊕], K[⊕], Ca²⁺, Mg²⁺, Al³⁺, etc. So reduction of H₂O occurs at cathode.
- ii. (x) Reduction potential of H₂O < (√) Reduction potential of other cations (than cations of 1, 2, and 13 group), e.g., Cu²⁺, Ag[⊕], Au³⁺, Cd²⁺, Zn²⁺, etc. So reduction of H₂O does not occur at cathode.
- iii. (\checkmark) Oxidation potential of $H_2O > (*)$ oxidation potential of F^{\odot} , SO_3^{2-} , SO_4^{2-} , NO_3^{\odot} , $S_2O_3^{2-}$, etc. So oxidation of H_2O occur at anode.
- iv. (*) Oxidation potential of H₂O < (✓) oxidation potential of Cl[©], Br[©], I[©], etc.

So oxidation of these ions occurs at anode.

Note:

- i. Although the oxidation potential of $H_2O > \text{oxidation}$ potential of Cl^{\odot} , so H_2O should get oxidized in preference to $Cl^{\odot}(aq)$. However on account of over potential of O_2 oxidation of Cl^{\odot} to Cl_2 is preferred at anode
- ii. In electrolysis, cations move towards cathode and anions move towards anode and the "chance" of their deposition/liberation depends on their electrode potential, concentration, over potential, etc.

3.12.2 QUANTITATIVE ELECTROLYSIS: FARADAY'S LAWS

First Law

It states that "the amount of any substance that is deposited of liberated at an electrode is directly proportional to the quantity of electricity passing through the electrolytic cell."

The amount of electricity means the quantity of charge (Q) in coulombs. If I is the current in amperes (A) and t is the time in seconds, then Q = It.

If W is the amount of substance liberated or deposited, then

Na Q

N= ZQ

7: Electrochemical equivalent of a substance

W = ZIt

second Law

when a given quantity of electricity is passed through Ment electrolytes, the amount of different substances produced the electrodes is directly proportional to their respective weights."

For two substances A and B in two different electrolytic cells:

$$\frac{W_{A}}{W_{B}} = \frac{(Ew)_{A}}{(Ew)_{B}}$$

vote: 1 g equivalent of a substance is deposited by passing Faraday of electricity.

Magnitude of charge carried by 1 mole of electrons is 96487 C $_{0.10^{23} \times 1.6 \times 10^{-19}} = 96487 \text{ C}$). It is also known as one faraday, $_{\rm is.l}$ F = 96500 C. [96500 C is the widely accepted value of 1 F]. Combining first and second law:

$$W \propto O$$

(First law)

 $W \propto E w$

(Second law)

$$\overline{W} = \frac{QEw}{F}$$
 $\left(\frac{1}{F} = \frac{1}{96500}\right) \Rightarrow \frac{W}{Ew} = \frac{Q}{F}$

Number of gram equivalents = Number of Faradays of electricity

⇒ 1 gEq of any substance = 1 F of electricity

There are three approaches to solve a problem.

a. First calculate the number of faradays of electricity by using:

Number of faradays =
$$\frac{Q}{F} = \frac{It}{96500}$$

b. Using the definition:

1 gEq of any substance $\equiv 1 \text{ F}$ of electricity passed

Calculate the number of gEq and by using the definition of gEq (gEq = W/Ew), determine the amount of substance deposited.

c. Using anodic and cathodic reactions as follows:

Let us consider a typical cathode reaction:

$$M^{n+} + ne^- \longrightarrow M$$

 $\Rightarrow n(e^-) \equiv 1$ molecule of $M \equiv 1$ ion of M^{n+}

 $\Rightarrow N_0(n e^-) \equiv N_0$ molecule of M $(N_0 : \text{Avogadro number})$

 $\Rightarrow N_0(n e^-) \equiv 1 \text{ mole of } M \equiv 1 \text{ mole of } M^{n+1}$

 $\Rightarrow nF \equiv 1 \text{ mole of } M \equiv 1 \text{ mole of } M^{n+1}$

(charge of N_0 electrons = 1 F = 96500 C)

So in this approach, first write anodic and cathodic reactions and derive the mole vs faraday relation.

For example:

$$Al^{3+} + 3e^{-} \longrightarrow Al$$

 \Rightarrow 3F = 1 mol of Al = 1 mole of Al³⁺ ions

$$2Cl^{\odot} \longrightarrow Cl_2 + 2e^{-}$$

⇒ $2F \equiv 1 \text{ mol of } Cl_2 \equiv 2 \text{ mol of } 2Cl^{\odot} \text{ ions}$

d. Using the combined relation obtained from first and second laws:

$$W = ZIt$$

$$\Rightarrow W = \frac{Ew.I.t}{96500}$$

3.12.3 CALCULATION OF pH OF THE SOLUTION **AFTER ELECTROLYSIS OF AQUEOUS SOLUTION OF A COMPOUND USING INERT ELECTRODE**

To calculate the pH or pOH, first calculate the concentration of H^{\oplus} or $\overset{\odot}{OH}$ ions by dividing the equivalent or mEq of these ions formed after electrolysis by the volume of the solution. The pH or pOH can then be calculated accordingly.

ILLUSTRATION 3.40

1 F of electricity is passed through 10 L of a solution of aqueous solution of NaCl. Calculate the pH of the solution.

Sol. Aqueous NaCl solution on electrolysis gives Cl₂(g) at anode and H₂(g) at cathode and OH ions in the solution.

1 F = 1 equivalent of
$$H_2(g) \equiv 1$$
 equivalent of $Cl_2(g)$

$$\equiv 1 \text{ Equivalent of OH ions}$$
∴ [OH] =
$$\frac{\text{Equivalent}}{\text{Volume of solution in L}} = \frac{1}{10 \text{ L}} = 10^{-1} \text{ N or M}$$

:.
$$pOH = -log(10^{-1}) = 1$$

$$pH = 14 - 1 = 13$$

ILLUSTRATION 3.41

A current strength of 96.5 A is passed for 10 s through 1 L of a solution of 0.1 M aqueous CuSO4. Calculate the pH of the solution.

Sol. Aqueous solution of CuSO₄ on electrolysis gives Cu at cathode and O_2 at anode and H^{\oplus} ions in the solution.

Eq of current =
$$\frac{96.5 \text{ A} \times 10 \text{ s}}{96500 \text{ C}} = 0.01 \text{ Eq} = 10^{-2} \text{ Eq}$$

:.
$$10^{-2}$$
 Eq of Cu = 10^{-2} Eq of $O_2 = 10^{-2}$ Eq of $H^{\oplus} = 10^{-2}$ F

$$\therefore [H^{\oplus}] = \frac{10^{-2} \text{ Eq}}{\text{Volume of solution in L}} = \frac{10^{-2} \text{ Eq}}{11}$$

$$= 10^{-2} \text{ N or M}$$

$$\therefore pH = -log(10^{-2}) = 2$$

ILLUSTRATION 3.42

In the electrolysis of 7.2 L aqueous solution of CuSO₄, a current of 9.65 A passed for 2 hours.

a. Calculate the weight of Cu deposited at cathode.

b. Calculate the volume of O₂ produced at anode at 27°C and 1 atm pressure.

c. Calculate the pH of the solution after electrolysis. [Atomic mass of Cu = 63 g]

Sol. First method

$$(CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-})$$

At cathode:

$$Cu^{2+} + 2e^{-} \longrightarrow Cu(s)$$

At anode:

$$2H_2O \longrightarrow O_2 + 4H^{\oplus} + 4e^{-}$$

(Since the oxidation potential of H₂O > oxidation potential of SO_4^{2-} , so oxidation of H_2O occurs at anode and SO_4^{2-} and H^{\oplus} ions remain in the solution to give an acidic solution).

Number of faradays =
$$\frac{I \times t}{96500 \text{ C}} = \frac{9.65 \text{A} \times 2 \times 3600 \text{ s}}{96500 \text{ C} \text{ mol}^{-1}}$$

= 0.72 F.

a. Now from cathode: $(Cu^{2+} + 2e^{-} \longrightarrow Cu)$

$$2e^- = 2 \text{ F} \equiv 1 \text{ mol of Cu} = 63 \text{ g of Cu}$$

$$0.72 \text{ F} = \frac{63 \text{ g} \times 0.72 \text{ F}}{2} = 22.68 \text{ g}$$

b. Now from anode: $(2H_2O \longrightarrow O_2 + 4H^{\oplus} + 4e^-)$.

$$4e^- = 4 \text{ F} \equiv 1 \text{ mol of O}_2$$

$$0.72 \text{ F} = \frac{1 \times 0.72}{4} = 0.18 \text{ mol}$$

Now using gas equation: PV = nRT

$$V = \frac{nRT}{P} = \frac{0.18 \times 0.082 \times 300}{1} = 4.428 \text{ L of O}_2$$

c. Now from anode $(2H_2O \longrightarrow O_2 + 4H^{\oplus} + 4e^-)$

$$4e^- = 4 \text{ F} = 4 \text{ mol of H}^{\oplus}$$

$$0.72 \text{ F} = \frac{4}{4} \times 0.72 = 0.72 \text{ mol of H}^{\oplus}$$

$$[H^{\oplus}] = \frac{\text{Mol}}{\text{Volume in L}} = \frac{0.72 \text{ mol}}{7.2 \text{ L}} = 10^{-1} \text{M}$$

$$\therefore pH = -\log [10^{-1}] = 1$$

Second method

a. At cathode:

1 F = 1 equivalent of Cu =
$$\frac{63}{2}$$
 g of Cu
0.7 F = $\frac{63}{2} \times 0.72 = 22.68$ g of Cu deposited

b. At anode:

1 F = 1 equivalent of
$$O_2$$

0.72 F = 0.72 equivalent of
$$O_2 = \frac{0.72}{4}$$

$$= 0.18 \text{ mol of } O_2$$

Since mol =
$$\frac{\text{Equivalent}}{n \text{ factor}} \text{ or } \frac{\text{Equivalent}}{\text{charge}} = \frac{0.72}{4}$$

 $20^{-2} \longrightarrow O_2 + 4e^- (n \text{ factor} = 4)$

Now for volume of O2, proceed as in first method

c. 1 F = 1 equivalent of H^{\oplus} ions.

0.72 F = 0.72 equivalent of H[⊕] = 0.72 mol of H[⊕]
[Since
$$n$$
 factor for H[⊕] $_{\approx |_{1}}$

$$\therefore [H^{\oplus}] = \frac{0.72 \text{ mol}}{7.2 \text{ L}} = 10^{-1} \text{ M}$$

$$\therefore pH = 1$$

ILLUSTRATION 3.43

How many grams of Cl₂(g) can be produced by the electrolysis of molten NaCl with a current of 5.5 A for 25 min?

[Atomic weight of C1 = 35.5 amul

Number of Faradays =
$$\frac{I \times t \text{ in seconds}}{96500 \text{ C}}$$
$$= \frac{5.5 \text{ s} \times 25 \times 60 \text{ s}}{96500 \text{ C}} = 0.085 \text{ F}$$

First method

Oxidation of Cl[⊙] at anode:

$$2C1^{\odot} \longrightarrow Cl_2 + 2e^{-}$$

$$2e^{-} = 2 \text{ F} = 1 \text{ mol Cl}_{2} = 71 \text{ g}$$

$$0.085 \text{ F} = \frac{71}{2} \times 0.085 = 3.017 \text{ g Cl}_2$$

Second method

1 F = 1 equivalent of
$$Cl_2 = \frac{71 \text{ g}}{Charge} = \frac{71}{2} \text{ g}$$

$$\therefore 0.085 \text{ F} = \frac{71}{2} \times 0.085 = 3.017 \text{ g Cl}_2$$

ILLUSTRATION 3.44

What is the volume of O₂ liberated at anode at STP in the electrolysis of CdSO₄ solution when a current of 2 A is passed for 8 min?

Sol. Aqueous CdSO₄
$$\xrightarrow{\text{Electrolysis}}$$
 Cd²⁺ + SO₄²⁻

Number of Faradays =
$$\frac{I \times t \text{ s}}{96500 \text{ C}} = \frac{2A \times 8 \times 60\text{s}}{96500 \text{ C}}$$
$$= 0.0099 \approx 0.001 \text{ F}$$

In aqueous solution, oxidation of H₂O takes place than that In aqueous so, since oxidation potential of H_2O > oxidation of SO_{4-1}^4 of SO_4^{2-} . So oxidation of H_2O at some of SO_4 . So oxidation of H_2O at anode occurs.

potential of
$$D = 4$$

$$2H_2O \longrightarrow O_2 + 4H^{\oplus} + 4e^-$$
anothod

First method
First method

$$4e^{-4}F \equiv 1 \mod O_2 = 22.4 \text{ L at STP}$$

$$\frac{4e^{-44}}{0.001} = \frac{22.4 L \times 0.001 F}{4 F}$$

$$= 0.056 L of O_2$$

Second method

$$_{1F} = 1$$
 equivalent of $O_2 = \frac{22.4 L}{4} O_2$

Equivalent of O₂

$$= \frac{\text{Volume of 1 mol of a gas}}{n \text{ factor}}$$

$$= \frac{22.4}{4} = 5.6 \text{ L O}_2$$

$$n \text{ factor for O}_2 = 4$$

$$2O^{2-} \longrightarrow O_2 + 4e^-$$

$$\therefore$$
 1 F = 5.6 L or O_2 at STP

$$0.001 \text{ F} = 5.6 \times 0.001 = 0.056 \text{ L O}_2$$

ILLUSTRATION 3.45

What weight of Ni is plated out in an electrolysis of aqueous NiSO₄ solution that it takes place to deposit 2 g of Ag in a silver coulometer that is arranged in series with NiSO4 electrolytic cell. [Atomic weight of Ag = 107.8 amu, atomic weight of Ni

[50]. Applying Faraday's second law of electrolysis,

$$\frac{W \text{ of Ni}}{W \text{ of Ag}} = \frac{Ew \text{ of Ni}}{Ew \text{ of Ag}}$$

$$W_{\text{Ni}} = \frac{W_{\text{Ag}} \times Ew \text{ (Ni)}}{Ew \text{ (Ag)}}$$

$$Ew \text{ of Ag} = \frac{\text{Atomic weight}}{n \text{ factor}}$$

$$= \frac{107.8}{1}$$

$$= \frac{2 \text{ g} \times 58.7/2}{107.8/1} \qquad \begin{bmatrix} Ew \text{ of Ni} = \frac{\text{Atomic weight}}{n \text{ factor}} \\ = \frac{58.7}{2} \end{bmatrix}$$

= 0.5445 g of Ni deposited

ILLUSTRATION 3.46

What is the amount of Al deposited on the electrolysis of molten Al₂O₃ when a current of 9.65 A is passed for 10.0 s.

Sol. Molten
$$Al_2O_3 \xrightarrow{Electrolysis} 2Al^{3+} + 3O^{2-}$$

Number of Faradays =
$$\frac{I \times t \text{ s}}{96500 \text{ C}}$$
$$= \frac{9.65 \text{ A} \times 10 \text{ s}}{96500 \text{ C}} = 10^{-3} \text{ F}$$

First method

Reduction of Al3+ at cathode

$$Al^{3+} + 3e^- \longrightarrow Al$$

$$3e^- = 3 \text{ F} = 1 \text{ mol Al} = 27 \text{ g Al}$$

$$\therefore 10^{-3} \, F = \frac{27}{3} \times 10^{-3} \, g$$

Second method

$$1 \text{ F} = 1 \text{ equivalent of Al} = \frac{1 \text{ mol}}{\text{Charge}} = \frac{27 \text{ g}}{3} = 9 \text{ g}$$

$$10^{-3} \text{ F} = 9 \times 10^{-3} \text{ g} = 0.009 \text{ g Al deposited}$$

ILLUSTRATION 3,47

Calculate the number of Faradays required to electrolyze 6.35 g of Cu[⊕](aq) ions from an aqueous solution.

Sol. Reduction of Cu[⊕] at cathode.

$$Cu^{\oplus} + 1e^{-} \longrightarrow Cu$$

$$1e^{-} = 1 \text{ F} = 1 \text{ mol of Cu} = 63.5 \text{ g of Cu}$$

$$\therefore 6.35 \text{ g of Cu will be deposited} = \frac{1 F \times 6.35 \text{ g}}{63.5 \text{ g}} = 0.1 \text{ F}$$
$$= 0.1 \text{ F}$$

ILLUSTRATION 3.48

100 mL of 0.3 M Fe3+(aq) ions were electrolyzed by a charge of 0.072 F. In electrolysis, metal was deposited and O₂(g) was evolved. At the end of electrolysis, it is desired to oxidize the un-electrolyzed metal ion.

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$$

$$Fe^{2+} + 2e^{-} \longrightarrow Fe$$

The moles of Fe²⁺ ions left un-electrolyzed in the solution is

- **b.** 0.021
- c. 0.072
- **d.** 0.042

Sol. a. mmoles of Fe³⁺ = $100 \times 0.3 = 30$

Charge =
$$0.072 \text{ F} = 0.072 \times 10^3 = 72 \text{ mF}$$

i.
$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$$

30 mmoles of Fe3+ requires 30 mF and 30 mmoles of Fe²⁺ formed.

ii. mF left =
$$72 - 30 = 42$$
 mF

iii.
$$Fe^{2^+} + 2e^- \longrightarrow Fe(s)$$

 $42 \text{ mF will electrolyze} = 21 \text{ mmol of } Fe^{2^+}$
 $[Since 2e^- = 2 \text{ F or } 2 \text{ mF} = 1 \text{ mmol of } Fe^{2^+}$
 $= 1 \text{ mmol of } Fe]$
 $\therefore \text{ mmoles of } Fe^{2^+} \text{ left} = 30 - 21 = 9 \text{ mmol}$
 $= 9 \times 10^{-3} = 0.009 \text{ mol}$

Marshall's acid $(H_2S_2O_8)$ or peroxo disulphuric acid is prepared by the electrolytic oxidation of H₂SO₄ as:

$$2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^{\oplus} + 2e^{-}$$

 $O_2(g)$ and $H_2(g)$ are obtained as byproducts. In such electrolysis $4.48 \text{ L of H}_2(g)$ and $1.12 \text{ L of O}_2(g)$ were produced at STP. The weight of H₂S₂O₈ formed is

Sol. b. Refer Section 3.13.1 (point h).

Aqueous
$$H_2SO_4$$
 Electrolysis $\rightarrow 2H^{\oplus} + SO_4^{2-}$ (dil or conc)

At anode, two reactions are competing:

i.
$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^{-}$$

ii.
$$H_2O \longrightarrow \frac{1}{2}O_2 + 2H^{\oplus} + 2e^{-}$$

At cathode, only one reaction occurs:

$$2H^{\oplus}$$
 (from H_2SO_4) + $2e^- \longrightarrow H_2(g)$

Since one reaction at cathode and two reactions at anode are taking place, therefore, the equivalent of H2(g) produced at cathode should be equal to the equivalent of O2(g) produced + equivalent of $H_2S_2O_8$ formed.

Note: Equivalent of
$$H_2 = \frac{\text{Given volume of}}{\text{Volume of 1 equivalent}}$$

of $H_2(g)$ at STP in L

$$= \frac{4.48 L}{22.4 L/2}$$
 (n factor for H₂ = 2)

Given volume of

Equivalent of
$$O_2 = \frac{O_2(g) \text{ in } L}{\text{Volume of 1 equivalent}}$$

of $O_2(g)$ at STP in L

$$= \frac{1.12 L}{22.4 L/4}$$
 (n factor for O₂ = 4)

Equivalent of
$$H_2S_2O_8 = \frac{W_{H_2S_2O_8}}{Ew \text{ of } H_2S_2O_8}$$

$$\begin{bmatrix} \text{Ew of } H_2 S_2 O_8 = \frac{Mw}{\text{n factor}} \\ = \frac{194}{2} \end{bmatrix}$$

 \therefore Equivalent of H₂ = Equivalent of O₂ + Equivalent of H₂S₂O₃

$$\frac{4.48}{22.4/2} = \frac{1.12}{22.4/4} + \frac{W_{\text{H}_2\text{S}_2\text{O}_8}}{194/2}$$

$$W$$

$$0.4 = 0.2 + \frac{W}{97}$$

$$\therefore W_{\rm H_2S_2O_8} = 19.4 \text{ g}$$

ILLUSTRATION 3.50

What volume of 0.2 M FeSO₄ can be oxidized by a current of 0.965 ampere hour? **b.** 0.08 L **c.** 0.09 L

Sol. c.
$$1 \text{ F} = 96500 \text{ C} = 1 \text{ equivalent of Fe}^{2+}$$

$$0.965 \times 3600 \text{ C} = \frac{0.965 \times 3600}{96500} = \frac{36}{1000} \text{ equivalent}$$

$$V(\text{in L}) \times N = \text{Equivalent}$$

(*n* factor
$$Fe^{2+} = 2$$
)

$$V(\text{in L}) \times 2 \times 0.2 = \frac{36}{1000}$$

$$V(\text{in L}) = \frac{36}{1000 \times 2 \times 0.2} = 0.09 \text{ L}$$

ILLUSTRATION 3.51

100 mL of 1 M solution of CuBr₂ was electrolyzed with a current of 0.965 ampere hour. What is the normality of the remaining CuBr, solution? **a.** 1.64 **b.** 3.28 **c.** 0.82 **d.** 4.92

Sol. a. Initial mEq of
$$Cu^{2+} = V(mL) \times N$$

= $100 \times 1 \times 2$

('n' factor for
$$Cu^{2+}=2$$
)

Electricity passed =
$$\frac{0.965 \times 3600}{96500}$$

$$= 36 \times 10^{-3} \text{ Eq}$$

$$= 36 \text{ mEq}$$

mEq of
$$CuBr_2$$
 remaining = $200 - 36 = 164$

$$N = \frac{\text{mEq}}{V \text{ (in mL)}} = \frac{164}{100} = 1.64$$

ILLUSTRATION 3.52

In a 500 mL of 0.5 M CuSO₄ solution, during electrolysis 1.5×10^{23} electrons with the solution of the 1.5×10^{23} electrons were passed using copper electrodes. Assume the volume of solution remains unchanged during electrolysis Which Co. electrolysis. Which of the following statements is/are correct?

- At the end of electrolysis, the concentration of the solution is 0.5 M.
- 7.9 g of Cu is deposited on the cathode.
- 4 g of Cu is dissolved from the anode.
- d. 7.9 g of Cu²⁺ ions are discharged.

Electrolysis of aqueous solution of CuSO₄ using Cu electrodes (active electrodes): Cu is dissolved at Cu anode elections and there is no change in the concentration of CuSO₄ solution.

concentration
$$= [Cu^{2+}]_{after} = 0.5 \text{ M}$$

 $: [Cu^{2+}]_{before} = [Cu^{2+}]_{after} = 0.5 \text{ M}$

So statement (a) is correct.

So statement (4)
moles of e-'s number of Faradays =
$$\frac{1.5 \times 10^{23}}{6 \times 10^{23}} = 0.25 \text{ F}$$

$$(Cu^{2+} + 2e^{-} \longrightarrow Cu)$$

$$\frac{(Cu^2 + 2e^2)}{2e^2} = 2F = 1 \text{ mol of } Cu^{2+}$$

$$2e^{-2}$$
 = 2F = 1 more of Cu²⁺ = 0.125 × 63.5 g
: 0.25 F = 0.125 mol of Cu²⁺ = 0.125 × 63.5 g

= 7.93 g of Cu is deposited on the cathode

So statement (b) is also correct.

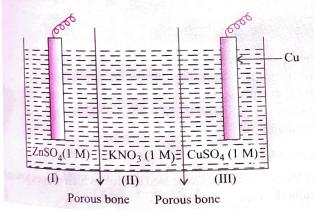
Same amount of Cu2+ ions are discharged from the solution to give same amount of Cu deposited at cathode.

So statement (d) is also correct.

Hence statements (a, b, and d) are correct.

ILLUSTRATION 3.53

Consider the following cell:



Given: Volume of solution in each compartment = 1 L.

$$E_{\text{Zn }^{2+}|\text{Zn}}^{\ominus} = -0.76 \text{ V}, E_{\text{Cu }|\text{Cu}^{2+}}^{\ominus} = -0.34 \text{ V}$$

Choose the correct statements regarding the above cell after passage of 0.1 F charge.

(Assuming that the current within the cell is carried equally by the positive and negative ions)

- Moles of Cu²⁺ ion reduced in compartment (III) is 0.05.
- **b.** $[SO_4^{2-}] = 0.975 \text{ M} \text{ in (III) compartment.}$
- c. $[NO_3^{\circ}] = 0.95 \text{ M in (II) compartment.}$
- d. Cu²⁺, K[⊕], and NO₃[⊙] ions are present in (II) compartment.

Effect of electrode: Oxidation of Zn to Zn2+ at anode (I compartment) and reduction of Cu2+ to Cu at cathode (III compartment) occurs by the passage of 0.1 F of electricity.

Effect by the migration of ions through porous bone: Since charge carried by positive or negative ions is equal, therefore the transport number of each ion is equal, i.e.,

$$t_{a} \odot = t_{c} \oplus = \frac{1}{1+1} = 0.5$$
. Hence, number of ions transported

from one compartment to another = $0.5 \times 0.1 \text{ F} = 0.05 \text{ Eq.}$

Note: There is no migration of ions of the solution when salt bridge is used. $E_{\text{cell}}^{\odot} = +0.34 - (-0.76) = 1.1 \text{ V. Hence}$ cell is spontaneous.

Sol. (a, b, c)

- a. Moles of Cu²⁺ reduced in compartment III is 0.05. Hence, correct.
- **b.** $[SO_4^{2-}] = 0.975 \text{ M}$ in compartment III. Hence, correct.
- c. $[NO_3^{\odot}] = 0.95 \text{ M}$ in compartment II. Hence, correct.
- **d.** Compartment II contains K^{\oplus} , NO_3^{\odot} , and Zn^{2+} ions. Hence, wrong.

	I compartment	II compartment	III compartment
Initial moles	$Zn^{2+} = 1 M \times 1 L = 1$ $SO_4^{2-} = 1 M \times 1 L = 1$	$K^{\oplus} = 1 M \times 1 L = 1$ $NO_3^{\ominus} = 1 M \times 1 L = 1$	$Cu^{2+} = 1 M \times 1 L = 1$ $SO_4^{2-} = 1 M \times 1 L = 1$
Effect of electrode	Formation of Zn^{2+} $Zn \longrightarrow Zn^{2+} + 2e^{-}$		Reduction of Cu^{2+} $Cu^{2+} + 2e^{-} \longrightarrow Cu$ $2e^{-} = 2 \text{ F} = 1 \text{ mol } Cu^{2+}$
	$2e^{-} = 2 \text{ F} = 1 \text{ mol } Zn^{2+}$ $0.1 \text{ F} = \frac{0.1}{2} = +0.05 \text{ mol } Zn^{2+}$		$0.1 \text{ F} = -0.05 \text{ mol Cu}^{2+}$

Positive ion movement	(For migration of Zn^{2+} ions) $\frac{0.1}{2} = 0.05Eq \text{ is taken}$ $\therefore \text{ For } 0.05F = \frac{-0.05}{2} \text{ mol}$ $= -0.025 \text{ mol } Zn^{2+}$ (Migrated to II compartment)	$+0.025 \text{ mol } Zn^{2+}$ $=+0.025 \times 2\text{Eq of } Zn^{2+}$ $=+0.05\text{Eq of } Zn^{2+}$ (migration of K^{\oplus} ions to III compartment) $K^{\oplus}=-0.05\text{Eq or mol}$	+0.05 mol K [⊕] From II compartment
Negative ion movement	+ve charge here So NO_3° migrated from II compartment = + 0.05 mol of NO_3°	NO_3^{\odot} migrated to I compartment For $\frac{0.1}{2}$ Eq = -0.05 mol NO_3^{\odot}	0.05
Final concentration (M)	$[Zn^{2+}]_{left} = +0.05 - 0.025$ = 0.025 M $[Zn^{2+}]_{Final} = Initial + left$ = (1 + 0.025) M = 1.025 M $[NO_3^{\odot}] = 0.05$ M	$[K^{\oplus}] = 1 - 0.05 = 0.05 \text{ M}.$ $[NO_3^{\odot}] = 1 - 0.05 = 0.95 \text{ M}$ $[Zn^{2+}] = 0.025 \text{ M}$	$[SO_4^{2-}]_{moved} = \frac{0.05}{2} = 0.025$ $[SO_4^{2-}]_{Final} = 1 - 0.025$ $= 0.975 \text{ M}$ $[Cu^{2+}]_{left} = 1 - 0.05$ $= 0.05 \text{ M}$ $[K^{\oplus}] = 0.05 \text{ M}$

ILLUSTRATION 3.54

A Zn rod weighing 1.0 g is taken in 100 mL of 1 M CuSO, solution. After some time, [Cu²⁺] in solution = 0.9 M (atomic weight of Zn = 65.5 g). Which of the following statements is/ are correct?

- a. 0.655 g of Zn was lost during the reaction.
- **b.** 0.327 g of Zn was lost during the reaction.
- c. There is no change in the molarity of SO_4^{2-} ion.
- **d.** There is a change in the molarity of SO_4^{2-} ion.

Sol. (a, c)

a. mEq. of Cu²⁺ before reaction

=
$$100 \times 1 \times 2$$
 (*n* factor for $Cu^{2+} = 2$)
= 200

mEq of Cu^{2+} after reaction = $100\times0.9\times2=180$

 $mEq ext{ of } Cu^{2+} ext{ lost} = 200 - 180 = 20$

mEq of Zn lost = 20

Weight of Zn lost = mEq \times 10⁻³ \times Ew of Zn

=
$$20 \times 10^{-3} \times \frac{65.5}{2}$$

(*n* factor for $Zn = 2$)
= 0.655 g

There is no change in the molarity of $SO_4^{\ 2-}$ ions, since SO₄²⁻ ions have not been oxidized and there is no change is the volume of solution.

ILLUSTRATION 3.55

A sodium salt of ternary acid of molybdenum (atomic mass = 96 has the formula Na₂MoO_n. When an acidified solution of Na₂MoO_n is electrolyzed, O₂ gas is liberated corresponding 10 a volume of 0.112 L at STP and 0.32 g of Mo is deposited. Find the formula of salt.

Sol.
$$Na_2MoO_n \longrightarrow 2Na^{\oplus} + MoO_n^{2-}$$

If MoO_n²⁻ ion gets dissociated to Mo^{x+} which moves toward cathode, then

$$1 F = 1 Eq of O_2 \equiv 1 Eq of Mo$$

Eq of
$$O_2 = \frac{\text{Volume of } O_2(\text{given}) \text{ in } L}{\text{Volume of one Eq of } O_2 \text{ in } L}$$

(*n* factor of $O_2 = 4$)

$$= \frac{0.112 \text{ L}}{22.4/4} = 0.02$$

Eq of Mo =
$$0.02 = \frac{W_{\text{Mo}}}{Ew_{\text{Mo}}}$$

$$\therefore 0.02 = \frac{0.32}{96/x}$$
(Let $n \text{ factor of Mo} = 0.02 = \frac{0.32}{96/x}$

$$\therefore x = 6$$

Reduction at cathode: $Mo^{x^+} + 6e^- \longrightarrow Mo$

 \therefore Oxidation state of Mo = 6

In Na2 MoOn, we have $\frac{1}{2(+1)^{+}} \frac{1}{6 + n} (-2) = 0$

 $_{\text{Molecular}}^{n}$ formula of $\text{Na}_{2}\text{MoO}_{n} \Rightarrow \text{Na}_{2}\text{MoO}_{4}$

LUSTRATION 3.56 is the quantity of electricity required to reduce 24.6 g calculate the quantity of aniline if the current efficiency is 75%. If of nitropental drop across the cell is 4.0 V, how much energy is Repotential drop of C.H. NO. = 123 g mol-1) the pure M_{w} of $C_6H_5NO_2 = 123 \text{ g mol}^{-1}$)

Half-cell reaction for the reduction of nitrobenzene to aniline is as below:

aniline is as below.

$$C_6H_5NO_2 + 6H^{\oplus} + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$$

$$C_6H_5NO_2 + 6H$$
 for $C_6H_5NO_2 + 6H$ for

Moles of Mass

$$6e^- = 6 \text{ F} = 1 \text{ mol of } C_6H_5NH_2$$

$$_{6e}^{-}$$
 = 6 F = 1 MoV 02 = 6, 3 = 2
0.2 mol of $C_6H_5NH_2 = 6 \times 0.2 = 1.2$ F

Hence, 1.2 F of electricity is used to reduce 24.6 g of nitrobenzene if the current efficiency is 100%.

But if the current efficiency is 75%, then

Number of Faradays required =
$$\frac{1.2 \text{ F} \times 100}{75}$$
$$= 1.6 \text{ F} = 1.6 \times 96500 \text{ C}$$

Now potential difference = 4.0 V

Energy (E) consumed = Charge × Potential difference $E = (1.6 \times 96500 \text{ C}) \times 4.0 \text{ V} = 617600 \text{ J} = 617.6 \text{ kJ}$

ILLUSTRATION 3.57

Find the volume of gases evolved by passing 0.1 A of current for 965 s, through an aqueous solution of sodium succinate at 27°C and 1 atm.

Reduction at anode of H₂O takes place.

$$2H_2O + 2e^- \longrightarrow 2OH + H_2\uparrow$$

[Since reduction potential of H₂O > reduction potential of Na[⊕]7

Total volume of gases evolved at STP = 4 mol

[1 mol of $C_2H_4 + 1$ mol of $H_2 + 2$ mol of CO_2]

2 F or 2 × 96500 C of electricity produces

= 4×22.4 L of gases at both electrodes at STP.

$$\therefore 0.1 \times 965 \text{ C will give} = \frac{4 \times 22.4}{2 \times 96500} \times 0.1 \times 965$$

= 44.8 mL

Volume at 27° C (300 K) and 1 atmosphere pressure

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
 \Rightarrow $\frac{44.8}{273} = \frac{V_2}{300}$

$$\therefore V_2 = \frac{44.8 \times 300}{273} = 49.23 \text{ mL}$$

ILLUSTRATION 3.58

A current strength of 1.0 A is passed for 96.5 s through 200 mL of a solution of 0.05 M KCl. Find

- The amount of gases produced
- b. The concentration of final solution w.r.t. OH ions
- c. pH of the solution

Sol.

a.
$$Cl^{\odot} \longrightarrow \frac{1}{2}Cl_2 + e^-$$
 (Anode)

$$H_2O + e^- \longrightarrow 2H_2 + OH$$
 (Cathode)

Electricity passed =
$$\frac{96.5 \times 1}{96500} = \frac{10^{-3}}{2}$$
 mol of e^{-}

$$\therefore 10^{-3} \text{ mol of } e^- \text{ produces } \frac{10^{-3}}{2} \text{ mol of } \text{Cl}_2$$

$$= \frac{10^{-3}}{2} \times 71 = 35.5 \times 10^{-3} \,\mathrm{g}$$

Also,
$$10^{-3}$$
 mol of e^- produces = $\frac{10^{-3}}{2}$ mol of H₂
= $\frac{10^{-3}}{2} \times 2 = 10^{-3}$ g

Total weight of gases = $10^{-3} \times 35.5 + 10^{-3} = 0.0365$ g

b.
$$[OH] = \frac{10^{-3} \text{ mol}}{200 \text{ mL (volume)}} = \frac{1 \text{ mmol}}{200 \text{ mL}} = 0.005 \text{ M}$$

c.
$$pOH = -log [0.005] = 2.3 \Rightarrow pH = 14 - 2.3 = 11.7$$

ILLUSTRATION 3.59

100 mL of CuSO₄ (aq) was electrolyzed using inert electrodes by passing 0.965 A current till the pH of the final solution was found to be 1. The solution after electrolysis was neutralized, treated with excess of KI, and titrated with 0.04 M Na₂S₂O₃ where 35 mL of it was used up. Assuming no change in the volume of solution. Find

- a. The time of electrolysis if the efficiency is 60%
- b. The initial concentration (in molarity) of CuSO₄

Sol.

a. pH = 1, [H^{\oplus}] = 0.1 M after *t* seconds

1000 mL contains 0.1 mol of H[⊕].

$$100 \text{ mL contains} = \frac{0.1 \times 100}{1000} = 0.01 \text{ mole of } H^{\oplus}$$

$$1 F = 1 \text{ mol of } H^{\oplus} = 1 \text{ Eq of } H^{\oplus}$$

 $0.01 \text{ F} = 0.01 \text{ mol of H}^{\oplus} = 0.01 \text{ Eq of H}^{\oplus}$

$$0.01 \times 96500 \text{ C} = \left(0.965 \times t \times \frac{60}{100}\right)$$

(Since 60% efficiency)

$$\therefore t = 1666.67 \text{ s} = 0.463 \text{ h}$$

b.
$$Cu^{2+} + KI \longrightarrow Cu_2I_2$$
 $(Cu^{2+} \longrightarrow Cu^{1+})$
 $mEq \text{ of } Na_2S_2O_3 = mEq \text{ of } I_2 = mEq \text{ of } Cu^{2+}$
 $\Rightarrow 0.041 \times 1 \times 35$
 $(2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-)$ $\left(n = \frac{2}{2} = 1\right)$

:. mEq of Cu²⁺ left in solution = 1.4 mEq
= 1.4 mmol
$$(n = 1)$$

$$(Cu^{2+} \longrightarrow Cu^{\oplus})$$

mol of Cu²⁺ deposited as Cu

$$(Cu^{2+} + 2e^{-} \longrightarrow Cu)$$

 $2 \text{ F} \Rightarrow 1 \text{ mol of Cu}^{2+}$ deposited as Cu

$$0.01 \text{ F} \Rightarrow \frac{1}{2} \times 0.01 = 0.005 \text{ mol}$$

So Cu²⁺ ions present initially = $0.005 + 1.4 \times 10^{-3}$ = 6.4×10^{-3} mols

Molarity =
$$\frac{\text{mols}}{\text{Volume in L}} = \frac{4 \times 10^{-3}}{100/1000} = 0.064 \text{ M}$$

ILLUSTRATION 3.60

A current of 5.0 A is passed through a 100 L aqueous solution of sodium succinate for 4.0 h. The gases produced at anode are collected separately at 25°C and 1.0 atm pressure. Find the volume of gases. Also find the pH of solution at the end of electrolysis. (Assume that at the start of electrolysis, pH of solution is 7.0 at 25°C)

Sol. At anode:
$$CH_2COO^{\odot} \longrightarrow CH_2 + 2CO_2 + 2e^-$$

$$CH_2COO^{\odot} \qquad CH_2$$

 $2 F = 1 \text{ mol of } (CH_2 = CH_2 + 2 \text{ mol of } CO_2)$

2 F = 3 mol of gases

Number of Faradays =
$$\frac{5 \times 4 \times 3600}{96500} = 0.746 \text{ F}$$

$${\text{moles of gases} \atop \text{at 25°C and 1 atm}} = \frac{3}{2} \times 0.746 \approx 1.12$$

$$= 1.12 \times 24.48 \text{ L}$$

$$= 27.4 \text{ L}$$

At cathode:

$$2H_2O + 2e^- \longrightarrow 2OH + H_2\uparrow$$

2 F = 2 mol of OH

$$0.746 \text{ F} = 0.746 \text{ mol of OH}$$

$$[\overset{\odot}{OH}] = \frac{0.746 \,\text{Eq}}{100 \,\text{L}} = 0.00746 \,\text{M} \text{ or N}$$

$$\therefore$$
 pOH = 2.13

$$pH = 14 - pOH = 11.87$$

ILLUSTRATION 3.61

A lead storage cell is discharged which causes H_2SO_4 electrolyte to change from a concentration of 40% by weight (density 1.25 g mL⁻¹ at 25°C) to one of 30% by weight. The original volume of electrolyte is 1 L. How many Faradays have left the anode of battery. Overall reaction of lead storage cell is:

$$Pb(s) + PbO_2 + 2H_2SO_4(1) \longrightarrow 2PbSO_4(s) + 2H_2O_4(s)$$

Sol. Weight of solution
$$(W_{sol}) = V_{sol}$$
 (in mL) × d_{sol}
= 1000 mL × 1.25 g mL⁻¹
= 1250 g

Weight of
$$H_2SO_4 = \frac{40 \times 1250}{100} = 500 \text{ g}$$

Weight of $H_2O = 1250 - 500 = 750 g$

After electrolysis,

Now during reaction, weight of H_2O formed = Xg

Moles of
$$H_2SO_4$$
 = moles of H_2O formed = $\frac{X}{18}$

(: mol ratio of $H_2SO_4 : H_2O = 1 : 1$)

Weight of
$$H_2SO_4$$
 used = $\frac{98X}{18} = 5.44X g$

 $[Mw \text{ of H}_2SO_4 = 98 \text{ g mol}^{-1}]$

Weight of
$$H_2SO_4$$
 left = $(500 - 5.44X)g$

% by weight of new solution

$$=\frac{(500-5.44X)}{(1250+X-5.44X)}=\frac{30}{100}$$

= 1250 + X - 5.44X

$$\therefore X = 30.43 \text{ g} = \frac{30.43}{18} \text{ mol of H}_2\text{O} \text{ are formed}$$

(Mol of
$$H_2O = Eq$$
 of H_2O) (: $2H_2O$ consumes $2e^{-1}$)

1 mol of H₂O formed by passage of 1 F.

$$\frac{30.43}{18}$$
 mol of H₂O formed = $\frac{30.43}{18}$ F = 1.69 F

JUSTRATION 3.62 density of copper is 8.95 g mL⁻¹. Find out the number of the number of the density needed to plate an area of 100 cm² to a third the density of corporate an area of 100 cm² to a thickness of solution as electrolyte. (Atom: The cm² to a thickness of cusing CuSO₄ solution as electrolyte. (Atomic weight 63.5 g)

$$|| cu||_{con}^{\text{poly}} || using || Cuse_4 || consisted || cuse_5 || cuse_6 || cuse_$$

$$= 100 \text{ cm}^3 \times 10^{-3}$$

$$= 1 \text{ cm}^3$$

$$= 1 \text{ cm}^{3}$$

$$\text{Weight of } Cu^{2+} \text{ deposited} = \text{Volume} \times \text{Density}$$

$$= 1 \text{ cm}^{3} \times 8.95 \text{ g mL}^{-1}$$

$$= 8.95 g$$

Now,
$$Cu^{2^+} + 2e^- \longrightarrow Cu$$

First method

First method

$$2e^{-}=2 \text{ F} \equiv 1 \text{ mol of Cu} = 63.5 \text{ g of Cu}$$

 $= 2 \text{ F}$

$$\equiv 2 \text{ F}$$

$$\equiv 2 \times 96500 \text{ C}$$

$$_{0.895}$$
 g of Cu = $\frac{2 \times 96500 \times 8.95}{63.5}$

$$W = \frac{Ew \times I(A) \times t \sec}{96500} \qquad (\because Q = It)$$

$$8.95 = \frac{63.5 / 2 \times Q}{96500} \implies Q = 27202.36 \text{ C}$$

Second method

$$1F = 1$$
 Eq of Cu

$$= \frac{63.5}{2}$$
 g of Cu

$$\frac{63.5}{2}$$
 g of Cu = 96500 C

LLUSTRATION 3.63

What is the (i) volume of gases evolved at STP and (ii) pH of solution on the electrolysis of 10 L of the following solutions when 1 F of electricity is passed:

- a. Aqueous solution of Na₂SO₄
- b. Aqueous solution of CH₃COONa
- c. Aqueous solution of HCOOK

Sol. a.

i. Since E^{\ominus}_{red} of $H_2O > E^{\ominus}_{red}$ of Na^{\oplus} ion.

and
$$E^{\odot}_{\text{oxid}}$$
 of $H_2O > E^{\odot}_{\text{oxid}}$ of SO_4^{2-} ion.

So the reduction and oxidation of H₂O takes place to give H₂ (cathode) and O₂ (anode), respectively.

$$H_2O + e^- \rightarrow OH + \frac{1}{2}H_2(g)$$

(Reduction)

$$H_2O \to \frac{1}{2}O_2(g) + 2H^{\oplus} + 2e^{-}$$

(Oxidation)

First method

At cathode:

At cathode.

$$1 e^- = 1 F = \frac{1}{2} \text{ mol of H}_2 = \frac{22.4}{2} L \text{ at STP}$$

 $= 11.2 L \text{ of H}_2$

At anode:

$$2e^{-} = 2 \text{ F} = \frac{1}{2} \text{ mol of O}_{2} = \frac{22.4}{2} \text{ L at STP}$$

$$\therefore 1 \text{ F} = \frac{22.4}{2 \times 2} = 5.6 \text{ L of O}_2$$

Total volume of gases at STP = 11.2 + 5.6 = 16.8 L

Second method

At cathode:

$$1 \text{ F} = 1 \text{ Eq H}_2 = \frac{22.4}{2} \text{ L} = 11.2 \text{ L H}_2$$

At anode:

$$1 \text{ F} = 1 \text{ Eq O}_2 = \frac{22.4}{4} \text{L} = 5.6 \text{L}$$

(*n* factor for $O_2 = 4$)

Total volume = (11.2 + 5.6) = 16.8 L

ii. pH of solution

Since OH ions are formed at cathode and H[⊕] ions are formed at anode. So they will remain in the solution and will neutralize to give neutral solution.

At cathode:

$$1 \text{ F} = 1 \text{ Eq OH}$$

$$\stackrel{\odot}{[OH]} = \frac{Equivalent}{Volume \text{ in } L} = \frac{1}{10} \text{ N or M}$$

At anode 1 F = 1 Eq of H^{\oplus}

or 2 F = 2 mol of H^{\oplus}

$$[H^{\oplus}] = \frac{1}{10} \text{ N or M}$$

Therefore, 0.1 M OH ion will neutralize 0.1 M H[⊕] ion to give neutral solution with pH = 7.

b.

i.
$$CH_3COONa(aq) \xrightarrow{Electrolysis} CH_3COO^{\odot} + Na^{\odot}$$

Since E_{red}^{\ominus} of $H_2O > E_{\text{red}}^{\ominus}$ of Na^{\oplus} ion, so reduction of water takes place at cathode to give $H_2(g)$.

At cathode:

$$H_2O + e^- \longrightarrow OH + \frac{1}{2}H_2 \uparrow$$

(Reduction)

At anode:

Kolbe's reaction:

$$2CH_3COO^{\circ} \longrightarrow 2CH_3COO^{\bullet} + 2e^{-}$$
 (Oxidation)

$$2CH_{3}COO^{\circ} \longrightarrow 2CH_{3}COO^{\bullet} + 2e^{-} \text{ (Oxidation)}$$

$$\downarrow \qquad \qquad \downarrow$$

$$CH_{3} - CH_{3} \uparrow \qquad \downarrow$$

At anode, the oxidation of $\mathrm{CH_3COO}^{\odot}$ takes place to give 2 mol of $CO_2(g)$ and 1 mol of ethane (C_2H_6) gas.

$$1e^- = 1 \text{ F} = \frac{1}{2} \text{ mol of H}_2 = \frac{22.4}{2} = 11.2 \text{ L of H}_2$$

At anode:

At anode.

$$2e^- = 2 \text{ F} = (2 \text{ mol of CO}_2 + 1 \text{ mol of C}_2 H_6)$$

$$\therefore$$
 2 F = 3 mol of gases

$$1 F = \frac{3}{2} \text{ mol of gases}$$
$$= \frac{3}{2} \times 22.4 \text{ Lat STP}$$

= 33.6 L at STP

Total volume of gases at STP =
$$(11.2 + 33.6)$$

= $44.8 L$

ii. pH of solution: Solution will be basic due to the formation of OH ions at cathode.

$$1e^{-}=1$$
 F = 1 Eq $\stackrel{\odot}{\text{OH}}$ ion,

$$\stackrel{\odot}{[OH]} = \frac{Equivalent}{Volume~in~L} = \frac{1~Eq}{10~L} = 10^{-1}~N~or~M$$

$$\therefore pOH = 1 \Rightarrow pH = 14 - 1 = 13$$

i.
$$HCOOK(aq) \xrightarrow{Electrolysis} HCOO^{\odot} + K^{\oplus}$$

Since E_{red}^{\ominus} of $H_2O > E_{\text{red}}^{\ominus}$ of K^{\oplus} ion, so reduction of H_2O takes place at cathode to give $H_2(g)$.

At cathode:

$$H_2O + e^- \longrightarrow OH + \frac{1}{2}H_2(g)$$
 (Reduction)

At anode: Kolbe's reaction

2HCOO^{$$\circ$$} → 2HCOO $^{\bullet}$ + 2 e^{-} (Oxidation)

$$\downarrow$$

$$H_{2}(g) \longleftarrow 2H^{\bullet} + 2CO_{2}(g) \uparrow$$

At anode, the oxidation of $HCOO^{\circ}$ takes place to give 1 mol of $H_2(g)$ and 2 mol of $CO_2(g)$.

At cathode:

$$1e^{-} = 1 \text{ F} = \frac{1}{2} \text{ mol of H}_2 = \frac{22.4}{2} = 11.2 \text{ L of H}_2$$

At anode:

$$2e^{-} = 2 \text{ F} = (1 \text{ mol of H}_{2} + 2 \text{ mol of CO}_{2})$$

$$2 F = 3 \text{ mol of gases}$$

$$1 F = \frac{3}{2} \text{ mol of gases}$$
$$= \frac{3}{2} \times 22.4 \text{ L at STP}$$
$$= 33.6 \text{ L at STP}$$

Total volume of gases at STP = 11.2 + 33.6

$$= 44.8 L$$

ii. pH of solution = 13 [Proceed as in part (b) (ii) above]

ILLUSTRATION 3.64

18.97 g fused SnCl₂ was electrolyzed using inert electrode. If nothing is 18.97 g fused Silver 1.187 g Sn was deposited at cathode. If nothing is obtained 1.187 g Sn was deposited at cathode of weight of second 1.187 g Sn was deposited at cathode. If nothing is obtained 1.187 g Sn was deposited at cathode. If nothing is obtained 1.187 g Sn was deposited at cathode. If nothing is obtained 1.187 g Sn was deposited at cathode. during electrolysis, calculate the ratio of weight of SnCl and during electrolysis. Given: SnCl₄ in fused state after electrolysis. Given:

Atomic weight of Sn = 118.7, Mw of SnCl₂ =189.7, Mw $SnCl_4 = 260.7$

Sol. Fused
$$SnCl_2$$
 Electrolysis \rightarrow $Sn^{2+} + 2Cl^{\odot}$

At cathode:
$$\operatorname{Sn}^{2+} + 2e^{-} \longrightarrow \operatorname{Sn}$$

(Reduction)

At anode:
$$2Cl^{\ominus} \longrightarrow Cl_2(g) + 2e$$

(Oxidation)

Further, Cl₂(g) formed at anode reacts with left over Sn() to give SnCl₄.

$$SnCl_2 + Cl_2 \longrightarrow SnCl_4$$

During electrolysis:

Eq of SnCl, lost = Eq of Cl₂ formed = Eq of Sn formed

Eq of
$$SnCl_2$$
 lost = Eq of Cl_2 formed
= Eq of $SnCl_4$ formed

= Eq of Sn formed
=
$$2 \times 10^{-2}$$

Now total loss is equivalent of SnCl, during complete cours = Eq of SnCl₂ lost during electrolysis

=
$$2 \times 10^{-2} + 2 \times 10^{-2} = 4 \times 10^{-2}$$

Eq of SnCl₂ (initially) = $\frac{18.97 \text{ g}}{189.7 / 2} = 2 \times 10^{-1}$

Eq of SnCl₂ left is molten solution

$$= 2 \times 10^{-1} - 4 \times 10^{-2} = 0.16$$

Eq of
$$SnCl_4$$
 formed = $2 \times 10^{-2} = 0.02$

$$\frac{\text{Weight of SnCl}_2 \text{ left}}{\text{Weight of SnCl}_2 \text{ left}} = \frac{\text{Weight of SnCl}_2 \text{ left}}{\times E \text{wof SnCl}_2}$$

$$= \frac{\text{Weight of SnCl}_2}{\text{Weight of SnCl}_4 \text{ formed}}$$

$$\times E \text{wof SnCl}_4$$

$$= \frac{(0.16 \times 189.7/2)}{(0.02 \times 260.7/2)} = 5.82$$

3.13 IONIC STRENGTH

The ionic strength (μ) of a solution is a measure of the electrical intensity due to the τ intensity due to the presence of ions in the solution. It is given as half of the sum of as half of the sum of all the terms obtained by multiplying concentration (molecules). concentration (molality) of each ion by the square of its valence.

Mathematically we be Mathematically, we have,

Ionic strength
$$(\mu) = \frac{1}{2} \sum c_i Z_i^2$$

$$= \frac{1}{2} \left(c_1 Z_1^2 + c_2 Z_2^2 + c_3 Z_3^2 + \cdots \right)$$

where c_1, c_2, c_3, \dots are the concentrations or molalities and Z_1, Z_2, \dots Z_3 are the valencies of the various ions present in the solution.

ILLUSTRATION 3.65

Calculate the ionic strength (μ) of the following electrolytes: 0.1 M or 0.1 m solution of KCl, CaCl₂, Na₃PO₄.

$$\mathbf{g.} \ \mu \left(\mathbf{K}^{\oplus} \, \mathbf{Cl}^{\ominus} \right) = \frac{1}{2} \sum_{i} c_{i} Z_{i}^{2} = \frac{1}{2} \left(c_{1} Z_{1}^{2} + c_{2} Z_{2}^{2} \right)$$
$$= \frac{1}{2} \left[0.1(1)^{2} + 0.1(-1)^{2} \right] = 0.1$$

b.
$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^{\odot}$$
Initial conc 0.1 m 0 0
Final conc .0 0.1 m $2 \times 0.1 = 0.2$ m

Molality of
$$Ca^{2+} = 0.1$$
, valency of $Ca^{2+} = 2$

Total molality of Cl^{Θ} ions = 0.2, valency of $Cl^{\Theta} = 1$

$$\therefore \mu \left(\text{CaCl}_2 \right) = \frac{1}{2} \sum_i c_i Z_i^2 = \frac{1}{2} \left(c_1 Z_1^2 + c_2 Z_2^2 \right)$$
$$= \frac{1}{2} \left[0.1(2)^2 + 0.2(1)^2 \right] = 0.3$$

c.
$$Na_3PO_4 \longrightarrow 3Na^{\oplus} + PO_4^{3-}$$
Initial conc 0.1 m 0 0
Final conc 0 $3 \times 0.1 = 0.3$ m 0.1 m

Valence of Na
$$^{\oplus}$$
 = 1, Molality of Na $^{\oplus}$ = 0.3

Valency of $PO_4^{3-} = 3$, molality of $PO_4^{3-} = 0.1$

$$\mu(\text{Na}_3\text{PO}_4) = \frac{1}{2} (c_1 Z_1^2 + c_2 Z_2^2) = \frac{1}{2} [0.3(1)^2 + 0.1(3)^2]$$

= 0.6

ILLUSTRATION 3.66

Calculate the ionic strength of 0.1 m KCl and 0.2 m K₂SO₄.

 $\begin{array}{ccc} K_2SO_4 & \longrightarrow & 2K^{\oplus} & + \\ 0.2 \text{ m} & & 0 & \end{array}$ Initial conc Final conc 0.2 m

 $2 \times 0.2 = 0.4 \text{ m}$

Total molality (m_1) of K^{\oplus} ion = 0.10 + 0.4 = 0.5

Charge (Z_1) of K^{\oplus} ion = 1

Total molality of Cl^{\odot} (m_2) = 0.1

Charge (Z_2) of Cl^{\odot} ion = 1

Total molality of SO_4^{2-} ion $(m_3) = 0.2$

Charge (Z_3) of SO_4^{2-} ion = 2

Hence, the ionic strength is:

$$\mu = \frac{1}{2} (c_1 Z_1^2 + c_2 Z_2^2) + c_3 Z_3^2$$

$$= \frac{1}{2} [0.5 (1)^2 + 0.1 (1)^2 + 0.2 (2)^2] = 0.7$$

ILLUSTRATION 3.67

Calculate the ionic strength of a solution made by mixing the equal volume 0.01 m KCl and 0.02 m AlCl₃.

Sol. After mixing [KCl] =
$$\frac{0.01 \text{ m}}{2}$$
 = 0.005 m

[Since equal volumes are mixed]

After mixing [AlCl₃] =
$$\frac{0.02}{2}$$
 = 0.01 m

$$\therefore [K^{\oplus}] = 0.005 \text{ m}, Z_1 = 1$$
[Al³⁺] = 0.01 m, $Z_2 = 3$,
[Cl^{\to]} = 0.005 (from KCl) + 3 × 0.01 (from AlCl₃)
= 0.035 m, $Z_3 = 1$

$$\mu = \frac{1}{2}(c_1Z_1^2 + c_2Z_2^2 + c_3Z_2^2)$$

$$= \frac{1}{2}[0.005(1)^2 + 0.01(3)^2 + 0.035(1)^2]$$
= 0.065

3.14 SOME COMMERCIAL CELLS (BATTERIES)

Although every spontaneous redox reaction can be used as the basis of an electrochemical cell, yet every such electrochemical cell is not suitable for commercial purposes. This is because of the following two reasons:

- a. Electrochemical cells using salt bridges have high internal resistance. As a result, if we try to draw large current from them, their voltage drops sharply.
- b. They lack the compactness and ruggedness (rough handling) for portability.

An electrochemical cell to be used as a commercial cell must fulfil the following two requirements:

- a. It should have the compactness, lightness, and ruggedness for portability.
- b. Its voltage should not drop much during use, i.e., drop in voltage should be negligible over the small interval of time during which it is being put to use.

If a number of cells are connected in series, the arrangement is called a battery. However, the term battery is sometimes used even for a single cell. Strictly speaking, such a usage is not correct.

Various commercial cells may be classified mainly into the following three types: (a) primary cells, (b) secondary cells, and (c) fuel cells.

Primary cells are those in which the redox reaction occurs only once and the cell becomes dead after some time, and cannot be used again. Two common examples of this type are dry cell and mercury cell.

Secondary cells are those which can be recharged by passing an electric current through them and hence can be used over and

again. Two well-known examples of this type are lead storage battery and nickel-cadmium storage cell.

Fuel cells are those in which the energy produced from the combustion of fuels such as H2, CO, CH4, etc., is directly converted into electrical energy. Such a conversion is possible because combustion reactions are also redox reactions.

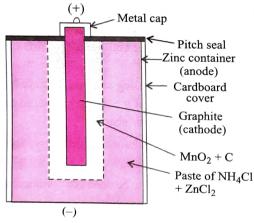
A brief description of the examples of each type is given below.

3.14.1 PRIMARY CELLS

Two main examples of primary celss are dry cell and mercury cell.

Dry Cell

A dry cell is a compact form of the Leclanche cell. It consists of a cylindrical zinc container which acts as the anode. A graphite rod placed in the centre (but not touching the base) acts as the cathode. The space between the anode and the cathode is so packed that the zinc container is in touch with the paste of NH₄Cl and ZnCl₂ and the graphite rod is fitted with a metal cap and the cylinder is sealed at the top with pitch. The zinc container is covered with cardboard to protect it from the atmosphere.



A commercial dry cell consists of graphite (carbon) cathode in Fig. 3.9 Zn container; the latter acts as the anode

The reactions taking place at the electrodes are quite complex. However, they can be represented approximately as follows:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$

At anode: $Zn (s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$ At cathode: $MnO_2 + NH_4 + e^{-} \longrightarrow MnO(OH) + NH_3$

 $2MnO_2(s) + 2NH_4^{\oplus}(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O$ (i.e., Mn has been reduced from oxidation state +4 to +3)

The NH₃ formed is not liberated as gas but combines immediately with Zn^{2-} ions and \rm Cl^{\odot} ions to form complex salt [Zn(NH₃)₄]²⁺Cl₂²⁻ (tetrammine zinc (II) chloride). These cells have voltage in the range 1.25 V to 1.50 V. However, they do not have a long life because the acidic NH₄Cl corrodes the zinc container even when the cell is not in use.

Mercury Cell

Mercury cell is used in small electrical devices such as hearing and container as the anode. Mercury cell is used in single and watches. It consists of zinc container as the anode, a carbon and watches. It consists mercuric oxide mixed with a container as the anode, a carbon and watches. rod as the cathode, and moist mercuric oxide mixed with Kolling and the two electrodes. A lining a the electrolyte filled between the two electrodes. A lining of porting and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the congrated from the zinc and a report of the zinc and a zinc and a zinc and a zinc and a zinc a zi paper keeps the electrolyte separated from the zinc anode. The collowing reactions produces electrical energy by the following reactions.

At anode:

$$Zn(Hg) + 2OH \longrightarrow ZnO(s) + H_2O(l) + 2e^{-l}$$

At cathode:

$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH$$

Overall reaction:

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

As the overall cell reaction does not involve any ion whose concentration may change, therefore this cell gives a constant potential of 1.35 V throughout its life. However, the spent cells should be reprocessed for mercury recovery or treated to prevent mercury or mercury compounds from entering the atmosphere and causing pollution.

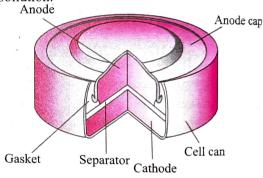


Fig. 3.10 Commonly used mercury cell. The reducing agent is zinc and the oxidizing agent is mercury(II) oxide

3.14.2 SECONDARY CELLS

Two main examples of secondary cells are lead storage batter, and nickel-cadmium storage cell.

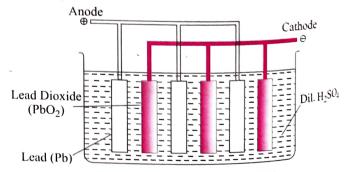


Fig. 3.11 Lead Storage battery of 6 V

Lead Storage Battery

This is one of the most common batteries used in the automobiles A 12-V lead store A 12-V lead storage battery generally consists of six cells each producing 2 V Each producing 2 V. Each cell consists of a lead anode (or a grid of lead filled with finely distributed) filled with finely divided spongy lead as the anode) and a grid of lead packed with lead in lead packed with lead dioxide as the cathode. These electrodes arranged alternately. arranged alternately, separated by thin wooden or fibre glass sheets

and suspended in dilute sulphuric acid (38% by mass or having a suspended in dilute sulphuric acid (38% by mass or having a suspended in dilute sulphuric acid (38% by mass or having a subject of 130 g cm⁻³) which acts as the alast-1. and suspense g cm⁻³) which acts as the electrolyte.

To increase the current output of each cell, the cathode plates joined together and the anode plates are also joined together Repling them in the alternate positions of course), i.e., the cells (keeping and cathode in parallel (anode to anode and cathode to cathode). To have an output voltage of 12 V, six cells are connected in series.

The electrode reactions that occur during discharge (i.e., when the external circuit is closed) are as follows:

At anode:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^{-}$$

At cathode:

$$PbO_2(s) + SO_4^{2-} + 4H^{\oplus}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$$

Overall reaction

$$Pb(s) + PbO2(s) + 4H⊕(aq) + 2SO42-(aq)$$

$$\longrightarrow 2PbSO4(s) + 2H2O$$

From the above equations, it is obvious that H₂SO₄ is used up during the discharge, As a result, the density of H₂SO₄ falls. When it falls below 1.20 g cm⁻³, the battery needs recharging.

During recharging, the cell is operated like an electrolytic cell, i.e., now electrical energy is supplied to it from an external source. The electrode reactions are the reverse of those that occur during discharge:

$$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$$

$$PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^{\oplus}(aq) + 2e^{-}$$

$$2PbSO_4(s) + 2H_2O \rightarrow Pb(s) + PbO_2(s) + 4H^{\oplus}(aq) + 2SO_4^{2-}(aq)$$

Such operation is possible because PbSO₄ formed during discharge is a solid and sticks to the electrodes. It is, therefore, in a position to either receive or give up electrons during electrolysis.

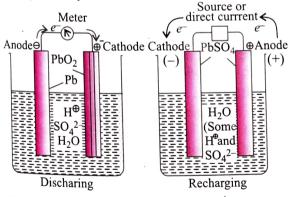


Fig. 3.12 Discharging and recharging of a lead storage cells

Nickel-Cadmium Storage Cell

This is another rechargeable cell which is becoming more and more popular especially in the calculators. It has a longer life than lead storage cell but is more expensive. It consists of a cadmium electrode (as anode) and a metal grid containing nickel (IV) oxide (as cathode) immersed in KOH solution. The electrode reactions occurring during discharge are as follows:

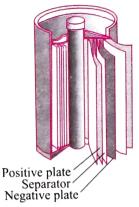


Fig. 3.13 A rechargeable nickel–cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydoxide

At anode:

$$Cd(s) + 2OH(aq) \longrightarrow Cd(OH)_2(s) + 2e^{-}$$

At cathode:

$$NiO_2(s) + 2H_2O + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH (aq)$$

Overall reaction

$$Cd(s) + NiO_2(s) + 2H_2O \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

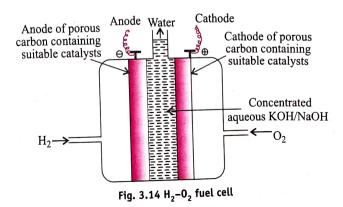
All the reactants and products in the overall reactions are in solid state.

As in the lead storage cell, the reaction products adhere to the electrodes. Hence, the reactions can be reversed during charging. Further as no gases are produced during discharging or recharging, the battery can be sealed.

The potential of each Ni–Cd cell is approximately 1.4 V.

3.14.3 FUEL CELLS

Galvanic cells that are designed to covert the energy produced during the combustion of fuels such as H2, CH4, CH3OH, etc., directly into electrical energy are called fuel cells. One such cell which has been very successful is the hydrogen-oxygen fuel cell. This cell was used as the primary source of electrical energy on the Apollo moon flights. The weight of the fuel sufficient for 11 days in space was approximately 200 kg. This may be compared with several ions that would have reacted. Moreover, the product of combustion, namely, water, was used for drinking by the astronauts.



3.54 Physical Chemistry

The general design of H_2-O_2 fuel cell is shown in Fig. 3.14. It consists of porous carbon electrodes containing suitable catalysts (finely divided Pt or Pd) incorporated in them for increasing the rate of electrode reactions. Concentrated KOH or NaOH solution is placed between the electrodes to act as the electrolyte. Hydrogen and oxygen gases are bubbled through the porous electrodes into the KOH/NaOH solution. Following electrode reactions take place:

At anode:
$$2H_2(g) + 4\overset{\odot}{OH}(aq) \longrightarrow 4H_2O(1) + 4e^{-}$$

At cathode:
$$O_2(g) + 2H_2O(1) + 4e^- \longrightarrow 4OH$$
 (aq)

Over reaction:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

(a) Advantages

Thus, gaseous materials are consumed and continuously supplied.

Because of the continuous supply, such cells never become dead. Such a cell is usually operated at a temperature of 70–140°C and gives a potential of about 0.9 V.

Theoretically, fuel cells are expected to have an efficiency of 100%. However, practically they give an efficiency of 60-70%. Still they are much superior to the thermal power plants in which fuels are burnt to produce heat which then changes water into steam to run the turbine. Such a power plant does not have efficiency of more than 40%. Another advantage of fuel cells is that they do not cause any pollution.

(b) Disadvantages

The construction of fuel cells is, however, faced with certain technical, economic, and practical difficulties. A few of these are as follows:

- a. Provision of contact between the three phases needed in a fuel cell, i.e., the gaseous fuel, the liquid electrolyte, and the solid catalyst.
- b. The corrosiveness of the electrolytes used.
- c. High cost of the catalysts needed for the electrode reactions (e.g., Pt, Pd, Ag, etc.)
- d. Problem of handling gaseous fuels at the low temperatures and high pressures.

3.15 CORROSION

The most common example of corrosion is the rusting of iron. Rust is hydrated ferric oxide, Fe₂O₃·xH₂O. Some other examples include tarnishing of silver, development of green coating on

3.15.1 MECHANISM OR THEORY OF CORROSION

The theory of corrosion can be explained by taking an example of the rusting of iron. The theory is called electrochemical theory because it explains the formation of rust on the basis of the formation of electrochemical cells on the surface of the metal.

The formation of rust on the basis of this theory may be explained in the following steps:

a. The water vapours on the surface of the metal dissolve The water vapours on the CO₂ and O₂ from the air. Thus, the surface of $metal_{ig}$ and $metal_{ig}$ and $metal_{ig}$ and $metal_{ig}$ and $metal_{ig}$ ${\rm CO_2}$ and ${\rm O_2}$ from the covered with the solution of ${\rm CO_2}$ in water, i.e., ${\rm carb_{0nic}}$ acid (H₂CO₃).

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

 $H_2O + CO_2$ This acts as an electrolytic solution of the cell. The carbonic acid and water dissociate to a small extent as follows.

$$H_2CO_3 \rightleftharpoons 2H^{\oplus} + CO_3^{2-}$$

$$H_2O \rightleftharpoons H^{\oplus} + \stackrel{\odot}{O}H$$

b. Iron in contact with dissolved CO_2 and oxygen undergoes oxidation as follows:

Fe(s)
$$\longrightarrow$$
 Fe²⁺ + 2e⁻ (E^{\odot}_{ox} = 0.44 V)

Thus, the sites where the above reaction takes place act as anodes. As a result of the above reaction, iron is converted into ferrous (Fe²⁺) ions.

c. The electrons lost by iron are taken up by the $H^{\oplus}_{i_{0}\eta_{i}}$ present on the surface of the metal which were produced by the dissociation of H_2CO_3 and H_2O . Thus, H^{\oplus} ions are converted into H atom.

$$H^{\oplus} + e^- \longrightarrow H$$

These H atoms either react with dissolved oxygen or oxygen from the air to form water.

$$4H + O_2 \longrightarrow 2H_2O$$
... (v

Multiplying Eq. (iv) with 4 and adding to equation (v), the complete reduction reaction may be written as

$$O_2 + 4H^{\oplus} + 4e^- \longrightarrow 2H_2O (E^{\ominus}_{red} = 1.23 \text{ V})$$

The dissolved oxygen may take up electrons directly to form

OH ions as follows:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH$$

The sites where the above reactions take place act is cathodes.

Adding Eqs. (iii) and (vi), the overall reaction of the miniature cell will be

$$2\text{Fe(s)} + \text{O}_2(g) + 4\text{H}^{\oplus}(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(l)$$

Note: It may be mentioned here that if water is saline, it helps in the flow of current in the miniature cell and hence enhances the process of corrosion.

d. The ferrous ions formed react with the dissolved oxygen of oxygen from the air to form ferric oxide as follows:

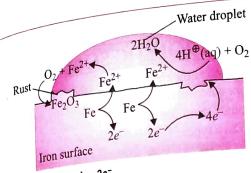
4Fe²⁺ + O₂ + 4H₂O
$$\longrightarrow$$
 2Fe₂O₃ + 8H ^{\oplus} (aq)
Ferric oxide there

Ferric oxide then undergoes hydration to form rust as follows:

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O$$
(hydrated for

(hydrated ferric oxide-rust)

It may be noted that the rust is a non-sticky compound i.e. it does not stick to the surface. It peels off exposing fresh iron surface for further rusting. The scheme of rusting is represented diagrammatically in Fig. 3.15.



Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ oridation: re(3) \rightarrow re (ay) + 2e Reduction: 0₂(9) + 4H[⊕](aq) + 4e⁻ \rightarrow 2H₂O(l) Reduction: $0_2(g)$ + 4π (eq.) + $2H_20(l)$ + $1/20_2(g)$ \rightarrow Fe $_20_3(s)$ + $4H^{\oplus}(aq)$ Atmospheric oxidation: $2\text{Fe}^{2+}(aq)$ + $2H_20(l)$ + $1/20_2(g)$

Fig. 3.15 Corrosion of iron in atmosphere

- Note: a. Since H^{\oplus} ions are involved in the reduction of O_2 . As the pH is increased or $[H^{\oplus}]$ is lowered, reduction of O_2 is less favoured. So Fe in contact with a solution whose pH is above 9-10 does not corrode.
 - b. Saline water helps in the flow of current in the miniature cell and increases corrosion. Therefore, in places where it snows heavily in winter and salting of roads is done, vehicles undergo greater rusting.
 - c. Rust is formed at a site other than the site where pitting has occurred, i.e., cathode is generally the area having the largest amount of dissolved O2, and the rust is often formed there.

3.15.2 FACTORS WHICH PROMOTE CORROSION

- a. Reactivity of the metal. More active metals are readily corroded.
- b. Presence of impurities. Presence of impurities in metals enhances the chances of corrosion. Pure metals do not corrode, e.g., pure iron does not rust.
- c. Presence of air and moisture. Air and moisture accelerate corrosion. Presence of gases such as SO_2 and CO_2 in air catalyze the process of corrosion. Iron when placed in vacuum does not rust.
- d. Strains in metals. Corrosion (e.g., rusting of iron) takes place rapidly at bends, scratches, nicks, and cuts in the metal.
- e. Presence of electrolytes. Electrolytes, if present, also increase the rate of corrosion. For example, iron rusts faster in saline water than in pure water.

3.15.3 PREVENTION OF CORROSION

Corrosion can be prevented by a number of ways. Some of these are explained below.

- a. Barrier protection: The metal surface is not allowed to come in contact with moisture, oxygen, and carbon dioxide. This can be achieved by the following methods:
 - i. The metal surface is coated with paint (or by some chemicals like bisphenol) which keeps it out of contact with air, moisture, etc., till the paint layer develops cracks.
 - ii. By applying a film of oil and grease on the surface of the iron tools and machinery, the rusting of iron can be prevented since it keeps the iron surface away from moisture, oxygen, and carbon dioxide.
 - iii. The iron surface is coated with non-corroding metals such as nickel, chromium, aluminium, etc. (by electroplating),

- or tin, zinc, etc. (by dipping the iron article in the molten metal). This again shuts out the supply of oxygen and water to iron surface.
- iv. The iron surface is coated with phosphate or other chemicals which give a tough adherent insoluble film which does not allow air and moisture to come in contact with iron surface.
- b. Sacrificial protection: Sacrificial protection means covering the iron surface with a layer of metal which is more active (electropositive) than iron and thus prevents the iron from losing electrons. The more active metal loses electrons in preference to iron and converts itself into ionic state. With the passage of time, the more active metal gets consumed but so long as it is present there, it will protect the iron from rusting and does not allow even the nearly exposed surface of iron to react. The metal which is most often used for covering iron with more active metal is zinc and the process is called galvanization. The layer of zinc on the surface of iron when comes in contact with moisture, oxygen, and carbon dioxide in air, a protective invisible thin layer of basic zinc carbonate ZnCO₃·Zn(OH)₂ is formed due to which the galvanized iron sheets lose their lustre and also tends to protect it from further corrosion.

Iron can be coated with copper by electro-deposition from a solution of copper sulphate or with tin by dipping into molten metal. Now if the coating is broken, iron is exposed and iron being more active than both copper and tin is corroded. Here iron corrodes more rapidly than it does in the absence of tin. At times, zinc, magnesium, and aluminium powders mixed with paints provide decorative protective coatings also.

c. Electrical protection/cathodic protection: The iron object to be protected from corrosion is connected to a more active metal either directly or through a wire. The iron object acts as cathode and the protecting metal acts as anode. The anode gradually disappears due to the oxidation of the metal to its ions due to loss of electrons. Hydrogen ions collect at the iron cathode and prevent the rust formation. The iron object gets protection from rusting as long as some of the active metal is present. Metals widely used for protecting iron objects from rusting are magnesium, zinc, and aluminium which are called sacrificial anodes.

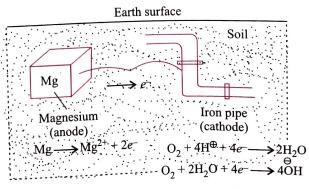


Fig. 3.16 Electrical protection of underground iron pipes

Magnesium is oftenly employed in the cathodic protection of iron pipes buried in the moist soil, canals, storage tanks etc. Pieces of magnesium are buried along the pipeline and connected to it by the wire as shown in Fig. 3.16.

d. Using anti-rust solutions: These are alkaline phosphate and alkaline chromate solutions. The alkalinity prevents the availability of hydrogen ions. In addition, phosphate tends to deposit an insoluble protective film of iron phosphate on the iron. These solutions are used in car radiators to prevent rusting of iron parts of the engine.

CONCEPT APPLICATION EXERCISE 3.2

- 1. A current of 40 microampere is passed through AgNO₃ solution for 19.3 min using platinum electrodes. 50% of cathode is occupied by a single-atom-thick silver layer. Calculate the total surface area of the cathode, if one silver atom occupies 5.5×10^{-16} cm² surface area.
- 2. Copper sulphate solution (250 mL) was electrolyzed using a platinum anode and a copper cathode. A constant current of 2 A was passed for 16 min. It was found that after electrolyses, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate to begin with.
- **3.** Ag | Ag[⊕] || Cu²⁺ | Cu The above cell initially contains 1 M Ag[⊕] and 1 M Cu²⁺ ions. Calculate the change in the cell potential after the passage of 9.65 A of a current for 1 hour.

Given: $E^{\odot}_{\text{Cu}^{2+}|\text{Cu}} = 0.34 \text{ V} \text{ and } E^{\odot}_{\text{Ag} \oplus |\text{Ag}} = 0.80 \text{ V}.$

- **4.** $E^{\ominus}_{Bi^{3+} \mid Bi}$ and $E^{\ominus}_{Cu^{2+} \mid Cu}$ are 0.226 V and 0.344 V, respectively. A mixture of salts of Bi3+ and Cu2+ at unit concentration each is electrolyzed at 298 K. To what value can [Cu²⁺] be brought down before bismuth starts to deposit during electrolysis?
- 5. 1 L aqueous solution of NaCl was electrolyzed between Pt electrodes by passing a direct current of 12.87 A for 100 s. With a current efficiency of 75%, calculate the pH of the solution after electrolysis assuming no change is the volume
- 6. The density of Cu is 8.94 g mL⁻¹. Determine the quantity of electricity required to electroplate an area $10 \, \text{cm} \times 10 \, \text{cm}$ to thickness of 10^{-2} cm using $CuSO_4$ as electrolyte.
- 7. a. In the following reactions, what weight of substance would be liberated if 1 F of electricity were passed through the cell:

i. $Cu^{2+} + 2e^{-} \longrightarrow Cu$

ii. $Al^{3+} + 3e^- \longrightarrow Al$

iii. $2C1^{\odot} \longrightarrow Cl_2 + 2e^-$

iv. $Ag^{\oplus} + e^{-} \longrightarrow Ag$

b. In the series of cathodes/anodes given above, how many coulombs are needed to produce 1 g of each of

i. Cu

ii. Al

iii. Cl₂

ANSWERS

1. 316.8 cm² 2. 0.08 M **4.** $[Cu^{2+}] = 10^{-4} M$

3. $E_{\rm cell}$ increases by 0.015 V

5. pH = 12

6. 27172 C

7. (a) (i) 31.75 g (ii) 9 g (iii) 35.5 g (iv) 108 g

(b) (i) 3039.4 C (ii) 10722.2 C (iii) 2718.3 C (iv) 893.5 C

3.16 CONDUCTANCE OF **ELECTROLYTIC SOLUTION**

Substances which allow electricity to pass through them are called Substances which do not allow electricity as conductors whereas substances which do not allow electricity as conductors whereas to pass through them are called as insulators. Conductors are divided into two types:

- a. Electronic conductors: Substance, which conduct electricity without undergoing any decomposition when current is passed are called electronic conductors, e.g., metals, graphite and certain minerals. The conductance is due to the f_{00W_0f} electrons. Graphite and certain minerals conduct electricity due to the presence of free electrons in them.
- b. Electrolytic conductors or electrolytes: Substances or solutions which conduct electricity and undergo decomposition when current is passed through them are called as electrolytic conductors or electrolytes, e.g., solution of acids, bases, and salts in water, molten, or fused salts etc. The flow of electricity is due to the movement of ions hence these are also called ionic conductance.

Electrolytes are classified as follows:

i. Strong electrolytes

ii. Weak electrolytes

iii. Non electrolytes

i. Strong electrolytes dissociate almost completely in aqueous solution or in the molten state and hence conduct electricity to a large extent. For example,

Strong acids: H₂SO₄, HCl, HNO₃, HClO₄, etc. Strong bases: KOH, NaOH, CsOH, Ca(OH)2, etc. Inorganic salts: NaCl, KCl, MgCl₂, CaCl₂, etc.

- ii. Weak electrolytes have low degree of dissociation and hence conduct electricity to a small extent, e.g., solution of sugar, urea, etc.
- iii. Non electrolytes do not conduct electricity at all. For example, solutions of most organic compounds.

3.16.1 FACTORS AFFECTING ELECTROLYTIC CONDUCTANCE

- a. Nature of electrolyte: Strong electrolytes ionize almost completely in the solution and hence conduct electricity to a large extent whereas weak electrolytes ionize to small extent and hence conduct electricity to a small extent.
- b. Concentration of the solution: More dilute (less concentration) a solution, more is the conductance. In a strong electrolyte, the inter ionic attractions are less at lower concentration whereas in a weak electrolyte, the degree of ionization increases on dilution. So with dilution, conductance increases.
- c. Temperature: The dissociation of electrolyte increases of increasing the control of the contr increasing the temperature and hence conductance increases.
- d. Nature of solvent: Greater the polarity of a solvent, greater is the ionizer. is the ionization, and hence greater is the conductance.
- e. Viscosity of solvent: Lesser is the viscosity of the solvent. greater is the conductance.

f. Size of the ions produced and their solvation: Greater is the ionic size, greater is the solvation of the ions (i.e., combination of the ions with the solvent), and hence less is the conductance.

3.16.2 FACTORS AFFECTING METALLIC OR ELECTRONIC CONDUCTANCE

The electrical conductance through metals depends upon:

- a. Nature and structure (i.e., electronic configuration) of the metal.
- b. Number of valence electrons per atom.
- c. Temperature of the metals as conductance decreases with the increase of temperature because on heating the positive ions of the metal atoms start vibrating and produce resistance (hindrance) in the flow of electrons.

Table 3.2 Difference between metallic conductors and electrolytic conductors

	Metallic conductors	Electrolytic conductors
a.	Conduct electricity without the decomposition of the substance.	Conduct electricity with the decomposition of the substance or electrolyte.
b.	The conductance decrease with the increase of temperature due to vibration of Kernels (positive ions) which produces resistance in the flow of electrons.	The conductance increases with the increase of temperature due to the increase in dissociation (or ionization) in cases of weak electrolyte and due to decrease in the inter-ionic attractions in strong electrolyte.
	Flow of electricity is due to the flow of electrons only, and not flow of matter. The conductance depends upon the structure, density, and number of valence elec- trons per atom of metal.	Flow of electricity is due to the movement of ions and hence there is flow of matter.
d.	The resistance is due to vibrating kernels.	The resistance is due to interionic attractions and viscosity of solvent.

3.16.3 RESISTANCE AND CONDUCTANCE OF SOLUTIONS

The hindrance provided by solution on the passage of current is called *resistance* and is represented by symbol R. Every substance offers resistance to the flow of electricity to a small or large extent. Resistance is calculated by *Ohm's law*. It states that if voltage V is applied to the ends of a conductor and current I flows through it, then R = V/I.

Current is generally measured in amperes, whereas voltage is measured in volts. If one ampere current flows through a conductor when a voltage of one volt is applied to it, the resistance of the conductor is 1 ohm (Ω) which in terms of SI base units is equal to $[(kg m^2)/(s^3A^2)]$

Thus, according to Ohm's Law,

$$\vec{R} = \frac{V}{I}$$
 or ohms = Volts/Amperes

or
$$\Omega = \frac{V}{A} = \frac{\text{Work per unit charge}}{A}$$
$$= \frac{\text{Work}}{\text{Charge}} \times \frac{1}{A} = \frac{F \times l}{A \times t} \times \frac{1}{A}$$
$$= \frac{m \times a \times l}{A^2 t} = \frac{\text{kg m s}^{-2} \times \text{m}}{A^2 \text{s}}$$
$$= (\text{kg m}^2)/(\text{s}^3 A^2)$$

Like metallic conductor, solutions of all electrolytes obey Ohm's law. Greater is the resistance provided by a substance, lesser will be the flow of electricity through it.

3.16.4 RESISTIVITY AND CONDUCTIVITY OF SOLUTIONS

Resistance can be measured with the help of a Wheatstone bridge. The electrical resistance of electrolytic solutions is directly proportional to its length (l) and inversely proportional to its area of cross section (a), i.e.,

$$R \propto \frac{l}{a} \Rightarrow \text{ or } R = \rho \frac{l}{a}$$

The constant of proportionality ρ (Greek, rho) is called resistivity (specific resistance). Its SI unit is ohm metre (Ω m) and quite often its submultiple, ohm centimeter (Ω cm), is also used. IUPAC recommends the use of the term resistivity over specific resistance.

Physically, the resistivity for a substance is its resistance (R) when it is 1 m (or 1 cm) long and its area of cross section is 1 m² (or 1 cm²), i.e.,

$$1\Omega$$
 m = 100Ω cm or 1Ω cm = 0.01Ω m
If $l = 1$ cm, and $a = 1$ cm², then $R = \rho$

Resistivity is defined as the resistance (R) of a conductor whose length is 1 cm (or 1 m) and area of cross section is 1 cm² (or 1 m²), i.e., it is the resistance of 1 cm³ of the conductor or in terms of SI units, it is the resistance of 1 m³ of the conductor.

The inverse of R is called conductance, G.

Thus,
$$G = \frac{1}{R} = \frac{a}{\rho l} = \kappa \times \frac{a}{l}$$
 (Since $R = \rho \frac{l}{a}$)

The SI unit of conductance is Siemens, represented by the symbol S and is equal to ohm⁻¹ (also known as mho) or Ω^{-1} .

The inverse of resistivity, called *conductivity* (specific conductance) is represented by the symbol κ (Greek, Kappa). IUPAC recommends the use of the term conductivity over specific conductance. The SI units of conductivity are S m⁻¹ or Ω^{-1} m⁻¹ or ohm⁻¹ m⁻¹ or mho m⁻¹, but quite often κ is expressed as S cm⁻¹.

Conductivity of a solution is defined as the conductance of a solution of 1 cm (or 1 m) length and its area of electrodes of 1 cm^2 (or 1 m^2).

Alternatively, it is defined as the conductance of 1 cm³ (or 1 m³) of the solution of electrolyte (see Fig. 3.17). The SI units are conductance of 1 m³ of the solution.

Thus, 1 S cm $^{-1}$ = 100 S m $^{-1}$

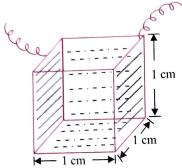


Fig. 3.17 Specific conductivity or conductivity

If the volume of the solution is $V \text{ cm}^3$, the conductivity of such a solution at this dilution V is written as κ_V . Similarly, at concentration c, it is represented as κ_c .

Units:

Resistivity (
$$\rho$$
) = $R \cdot \frac{a}{l}$
= $ohm \cdot \frac{(cm^2)}{cm}$
= $ohm cm or \Omega cm or \Omega m$ (SI units)

Conductivity (or specific conductivity) (κ) =

$$\begin{split} \frac{1}{\rho} &= \frac{1}{ohm \ cm} \ = ohm^{-1} \ cm^{-1} \ or \ \Omega^{-1} \ cm^{-1} \\ &= S \ cm^{-1} \ or \ S \ m^{-1} \ (SI \ units) \end{split}$$

Note: Conductivity is an additive property but resistance is not.

3.16.5 EQUIVALENT CONDUCTIVITY, MOLAR CONDUCTIVITY, AND CELL CONSTANT

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient. It is therefore necessary to define more meaningful quantities called equivalent and molar conductivities.

Equivalent conductivity of a solution at a dilution V is defined as the conductance of all the ions produced from 1 g equivalent of an electrolyte dissolved in $V \, \mathrm{cm}^3$ of the solution when the distance between the electrodes is 1 cm and the area of the electrodes is so large that whole of the solution is contained between them. It is represented by $\Lambda_{\rm eq}$ (lambda). Thus, mathematically,

$$\Lambda_{\rm eq} = \kappa \times V = \frac{\kappa \times 1000 \text{ cm}^3}{N} \text{ ohm}^{-1} \text{ cm}^2 \text{ Eq}^{-1}$$

where $\Lambda_{\rm eq}$ is the equivalent conductance (in ${\rm ohm^{-1}}_{\rm cm^2}$ eq⁻¹) of the solution at dilution V, κ = specific conductance of the solution at dilution V, V is the volume of the solution in cm³ containing 1 g equivalent of the electrolyte, and N is the normality of the solution. Thus, the formula along with units of each quantity is:

$$\Lambda_{\text{eq}}(\text{S cm}^2 \text{ Eq}^{-1}) = \frac{\kappa (\text{S cm}^{-1}) \times (1000 \text{ cm}^3 \text{L}^{-1})}{N (\text{g eq L}^{-1})}$$

Units:

$$\Lambda_{eq} = \kappa \times V = ohm \text{ cm}^{-1} \times \frac{\text{cm}^3}{\text{g Eq}}$$

$$= ohm^{-1} \text{ cm}^2 \text{ (g Eq}^{-1})$$

$$= \Omega^{-1} \text{ cm}^2 \text{ Eq}^{-1}$$

$$= \text{S cm}^2 \text{ eg}^{-1}$$

$$= \text{S m}^2 \text{ Eq}^{-1} \text{ (SI units)}$$

$$1 \text{ S m}^2 \text{ Eq}^{-1} = 10^4 \text{ S cm}^2 \text{ Eq}^{-1}$$

In terms of SI units, the Λ_{eq} is:

$$\Lambda_{\rm eq} = ({\rm S} \ {\rm m}^2 \ {\rm Eq}^{-1}) = \frac{\kappa ({\rm S} \ {\rm m}^{-1})}{N ({\rm g} \ {\rm Eq} \ {\rm m}^{-3})}$$

Note: There is no multiplication with 1000.

N is expressed in g Eq L^{-1} .

Thus,

$$\Lambda_{\rm eq} ({\rm S m^2 Eq^{-1}}) = \frac{\kappa ({\rm S m^{-1}})}{N ({\rm g Eq L^{-1}}) \times 1000 \,{\rm L m^{-3}}}$$

Molar conductivity of a solution at a dilution V is the conductance of all ions produced from one mole of the electrolyte dissolved in $V \, \mathrm{cm}^3$ of the solution when the electrodes are $1 \, \mathrm{cm}$ apart and the area of the electrodes is so large that the whole of the solution is contained between them. It is usually represented by Λ_{m}

$$\Lambda_{\rm m} = \left(\frac{\kappa \times 1000}{M}\right) \text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

where $\Lambda_{\rm m}$ is molecular (or molar) conductance (in ohm⁻¹ cm⁻¹ mole⁻¹) at dilution V, κ is the specific conductance of the solution at dilution V, V is the volume of the solution in cm³ containing 1 mole of the electrolyte, and M is the molarity of the solution. Units: Comparing with $\Lambda_{\rm eq}$, the units of $\Lambda_{\rm m}$ will be ohm⁻¹ cm⁻¹ mol⁻¹ or S cm² mol⁻¹ or S cm² mol⁻¹ (SI units)

1 S m² mol⁻¹ =
$$10^4$$
 S cm² mol⁻¹
1 S cm² mol⁻¹ = 10^{-4} S cm² mol⁻¹

Thus, the formula along with units of each quantity is:

$$\Lambda_{\rm m}({\rm S~cm^2~mol^{-1}}) = \frac{\kappa \, ({\rm S~cm^{-1}}) \, (1000 \, {\rm cm^3 L^{-1}})}{M \, ({\rm mol~L^{-1}})}$$

In terms of SI units, the formula is:

$$\Lambda_{\rm m} ({\rm S} \ {\rm m}^2 \ {\rm mol}^{-1}) = \frac{\kappa ({\rm S} \, {\rm m}^{-1})}{M \ ({\rm mol} \ {\rm m}^{-3})}$$

Note: There is no multiplication with 1000.

$$\Lambda_{\rm m} ({\rm S} \ {\rm m}^2 \ {\rm mol}^{-1}) = \frac{\kappa ({\rm S} \ {\rm m}^{-1})}{{\rm M} \ ({\rm mol} \ {\rm m}^{-3}) \times 1000 \ {\rm L} \ {\rm m}^{-3}}$$

Relationship between molar and equivalent conductivities

If $(v_+ z_+)$ or $(v_- z_-)$ is the total charge of cations (or anions) of a single electrolyte, it follows that

$$1 \text{ mol} = (v_+ z_+) (1 \text{ equivalent})$$

Hence,
$$\Lambda_{\rm m} = \frac{\kappa}{M}$$
, $\Lambda_{\rm eq} = \frac{\kappa}{N}$

$$N = n$$
 factor $\times M$

of
$$N = (v_+ z_+) \times M$$

= Total charge (cation or anion) $\times M$

$$\Lambda_{\text{eq}} = \frac{\kappa}{(\nu_+ z_+) \times M} = \frac{\Lambda_m}{(\nu_+ z_+)}$$

$$\Lambda_{\text{eq}} = \frac{\Lambda_{\text{m}}}{\text{Total charge of cations (or anions)}}$$

or

$$\Lambda_{\rm m} = \Lambda_{\rm eq} \times \text{Total charge of cations (or anions)}$$

Cell constant: The quantity $\frac{l}{a}$ is called cell constant and is denoted by the symbol G^* . It depends on the distance between electrodes and their area of cross section and has the dimension of length⁻¹ and can be calculated by knowing the value of l and a. The measurement of l and a is inconvenient and unreliable. It is determined by measuring the resistance (R) of the cell containing a solution whose conductivity is already known.

KCl is generally used for this purpose, whose conductivity is known accurately at various concentrations and at different temperatures. The cell constant G^* is given by

$$G^* = \frac{l}{a} = R\kappa$$

$$\kappa = \frac{G^*}{R} \text{ or } G^* G \qquad \text{(Since } l/R = G = \text{conductance)}$$

Specific conductance = Cell constant $(G) \times Conductance$ (G).

Units:
$$G^* = \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1} \text{ or m}^{-1} \text{ (SI units)}$$

3.16.6 MEASUREMENT OF THE CONDUCTIVITY OF IONIC SOLUTIONS

Accurate measurement of an unknown resistance can be performed on a Wheatstone bridge. In finding the resistance of the solution of an electrolyte (an ionic solution), there occur two problems.

Firstly, passing direct current (DC) changes the composition of the solution, i.e., electrolysis of the solution occurs. As a result, the concentration of the electrolyte near the electrodes changes resulting in the change of the resistance of the solution. This effect is called *polarization effect*.

This problem is resolved by using an alternating current (AC) source of power in the audio frequency range of 550 -5000

cycles per seconds (or Hertz, Hz). The source of AC is either an induction coil or a vacuum tube oscillator which is quieter and gives more symmetrical current. However, when AC is used, ordinary galvanometer fails to detect the null point. Hence, the galvanometer is replaced by earphone as the detector. Further, to minimize the polarization effects, the electrodes are coated with platinum black, i.e., finely divided platinum deposited on the electrodes electrolytically.

Secondly, a solution cannot be connected to the bridge like a metallic wire or any solid conductor. This problem is solved by using a specially designed vessel called conductivity cell. It is made up of pyrex glass and two platinum electrodes at a fixed distance apart.

The two platinum electrodes coated with Pt-black are separated by distance l, having area of cross section equal to a. Therefore, solution confined between these electrodes is a column of length l and area of cross section a. The resistance of such a column of solution is given by:

$$R = \rho \frac{l}{a} = \frac{1}{\kappa} \times \frac{l}{a} = \frac{1}{\kappa} \times G^*$$
 (G* = cell constant)

Once the value of cell constant (G^*) is determined by measuring the resistance of the cell containing a solution of KCl, whose conductivity is known, it is used for measuring the resistance (R) or conductivity (κ) of any solution, by using Wheatstone bridge (Figs. 3.18 and 3.19).

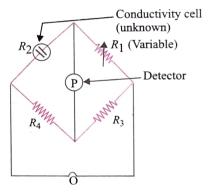


Fig. 3.18 Arrangement for measuring the resistance of the solution of an electrolyte

A Wheatstone bridge consists of two resistances R_3 and R_4 , a variable resistance R_1 and the conductivity cell having the unknown resistance R_2 . The Wheatstone bridge is connected by an oscillator O (a source of AC power in the audio frequency range of 550 to 5000 cycles per second). P is a suitable detector (a head phone or an earphone or other electronic device), and the bridge is balanced when no current passes the detector called null point.

When null point is obtained,
$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

Unknown resistance,
$$R_2 = \frac{R_1 R_4}{R_3}$$

Knowing the values of R_1 , R_3 , and R_4 , R_2 can be calculated. Nowadays, inexpensive conductivity metres are available which can directly read the conductance or resistance of the solution in the conductivity cell.

Alternate method

The complete assembly for the measurement of the electrolytic conductance is shown in (Fig. 3.19).

A suitable value of the resistance (R) is introduced from the standard resistance box such that when the jockey (i.e., sliding contact) is moved along the stretched wire, the sound in the earphone is reduced to the minimum, say at the point B. If X is the resistance of the electrolytic solution, by Wheatstone bridge principle, then

$$\frac{\text{Resistance } X}{\text{Resistance of wire BC}} = \frac{\text{Resistance of wire BC}}{\text{Resistance of wire AB}}$$
$$= \frac{\text{Length BC}}{\text{Length AB}}$$

Resistance
$$X = \text{Resistance } R \times \frac{\text{Length BC}}{\text{Length AB}}$$

Thus, knowing the resistance R and the balance point B, the resistance X of the electrolytic solution can be calculated. Thus,

Conductance,
$$G = \frac{1}{X} = \frac{1}{R} \times \frac{\text{Length AB}}{\text{Length BC}}$$

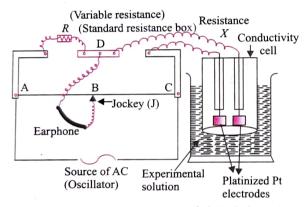


Fig. 3.19 Assembly for the measurement of electrolytic conductance

Once the cell constant and the resistance of the solution in the cell is determined, the conductivity (specific conductance) (κ) is calculated as

$$\kappa = \frac{\text{Cell constant}}{R} = \frac{G^*}{R} = \frac{1}{R} \times \frac{l}{a} = G \times \frac{l}{a}$$

Once κ is calculated, then Λ_{eq} and Λ_{m} are calculated by the expression

$$\Lambda_{\text{eq}} = \frac{\kappa \times 1000}{N}, \ \Lambda_{\text{m}} = \frac{\kappa \times 1000}{M}$$

Conductivity water: For accurate results, the solutions should be prepared in a specially purified water whose own conductance is very small. Such water is called conductivity water.

Alternatively, to get the resistance of the electrolyte, the resistance of water used for making the solution is determined and then subtracted from the resistance of the solution.

ILLUSTRATION 3.68

The resistance of a conductivity cell filled with 0.1 M KCl solution is 100 Ω . If R of the same cell when filled with 0.02 M KCl solution is 520 Ω , calculate the conductivity and molar conductivity of 0.02 M KCl solution. The conductivity of 0.1 M KCl solution is 1.29 S m⁻¹.

Sol. Cell constant,
$$G^* = \text{Conductivity} \times \text{Resistance}$$

= 1.29 S m⁻¹ × 100 Ω
= 129 m⁻¹ = 1.29 cm⁻¹
Conductivity (κ) of 0.02 M KCl solution = $\frac{G^*}{R}$
= $\frac{129 \text{ m}^{-1}}{520 \Omega}$
= 0.248 m⁻¹

$$\begin{aligned} Concentration &= 0.02 \ M = 1000 \times 0.02 \ mol \ m^{-3} \\ &= 20 \ mol \ m^{-3} \end{aligned}$$

Molar conductivity (
$$\Lambda_{\rm m}$$
) = $\frac{\kappa}{c} = \frac{0.248 \,\mathrm{S m}^{-1}}{20 \,\mathrm{mol m}^{-3}}$
= $124 \times 10^{-4} \,\mathrm{m}^2 \,\mathrm{mol}^{-1}$

Alternatively

$$\kappa = \frac{1.29 \text{ cm}^{-1}}{520 \Omega} = 0.248 \times 10^{-2} \text{ S cm}^{-1}$$
and
$$\Lambda_{\text{m}} = \frac{\kappa \times 1000 \text{ cm}^{3} \text{ L}^{-1} \text{ M}^{-1}}{M}$$

$$= \frac{0.248 \times 10^{-2} \text{ S cm}^{-1} \times 1000 \text{ cm}^{3} \text{ L}^{-1}}{0.02 \text{ M}}$$

$$= 124 \text{ S cm}^{2} \text{ mol}^{-1}$$

ILLUSTRATION 3.69

The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity, and molar conductivity.

Sol. Area
$$(a) = \pi r^2 = 3.14 \times \left(\frac{1 \text{ cm}}{2}\right)^2$$

 $= 0.785 \text{ cm}^2$
 $= 0.785 \times 10^{-4} \text{ m}^2$
 $l = 50 \text{ cm} = 0.5 \text{ m}$
 $R = \frac{\rho l}{a} \text{ or } \rho = \frac{Ra}{l} = \frac{5.55 \times 10^3 \text{ ohm} \times 0.785 \text{ cm}^2}{50 \text{ cm}}$
 $= 87.135 \text{ ohm cm}$
Conductivity $(\kappa) = \frac{1}{\rho} = \left(\frac{1}{87.135}\right) \text{S cm}^{-1} = 0.01148 \text{S cm}^{-1}$
Molar conductivity $(\Lambda_{\text{m}}) = \frac{\kappa \times 1000}{M} \text{ cm}^3 \text{ L}^{-1}$
 $= \frac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}}$
 $= 229.6 \text{ S cm}^2 \text{ mol}^{-1}$

Alternatively

The values of different quantities in SI units (i.e., in terms of "m" instead of "cm")

$$\rho = \frac{Ra}{l} = \frac{5.55 \times 10^3 \text{ ohm} \times 0.785 \times 10^{-4} \text{ m}^2}{0.5 \text{ m}}$$
$$= 87.135 \times 10^{-2} \text{ ohm m}$$

$$\kappa = \frac{1}{\rho} = \frac{100}{87.135} \text{ ohm}^{-1} \text{m}^{-1} = 1.148 \text{ S m}^{-1}$$

and
$$\Lambda_{\rm m} = \frac{\kappa}{c} = \frac{1.148 \,{\rm Sm}^{-1}}{50 \,{\rm mol}\,{\rm m}^{-3}} = 229.6 \times 10^{-4} \,{\rm S} \,{\rm m}^2 \,{\rm mol}^{-1}$$

ILLUSTRATION 3.70

The resistance of 0.01 N solution of an electrolyte is 210 Ω at 298 K with a cell constant of 0.88 cm⁻¹. Calculate the conductivity and equivalent conductivity of the solution.

$$R = 210 \text{ ohm}, \quad \frac{l}{a} = 0.88 \text{ cm}^{-1}$$

$$\kappa = \frac{1}{R} \times \frac{l}{a} = \frac{1}{210} \times 0.88 = 4.19 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \text{ or S cm}^{-1}$$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{4.19 \times 10^{-3} \times 1000}{0.01}$$

$$= 419.05 \text{ S cm}^2 \text{ eg}^{-1}$$

LLUSTRATION 3.71

The resistance and conductivity of 0.02 M KCl solution are 82.4 ohm and 0.002768 S cm $^{-1}$, respectively. When filled with 0.005 N $\rm K_2SO_4$, the solution had a resistance of 324 ohm. Calculate:

- a. Cell constant
- b. Conductance of K2SO4 solution
- c. Conductivity of K2SO4 solution
- d. Equivalent conductivity of K₂SO₄ solution
- e. Molar conductivity of K2SO4 solution

SA

a. From KCl data:
$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

$$\therefore \frac{l}{a} \text{ (cell constant)} = \kappa \times R = 0.002768 \times 82.4$$

$$= 0.2281 \text{ cm}^{-1}$$

From K₂SO₄ data:

b.
$$R = 324$$
 ohm, $G = \frac{1}{R} = \frac{1}{324} = 3.086 \times 10^{-3} \text{ S}$

c.
$$\kappa = G \times \frac{l}{a} = 3.086 \times 10^{-3} \times 0.2281$$

= 7.04 × 10⁻⁴ S cm⁻¹

d.
$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{7.04 \times 10^{-4} \times 1000}{0.005}$$

= 140.8 S cm² eq⁻¹

e.
$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M} = \frac{7.04 \times 10^{-4} \times 1000}{0.005 / 2}$$

= 281.6 S cm² mol⁻¹
[n factor for K₂SO₄ = 2; M = N/2]

ILLUSTRATION 3.72

The resistance of decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4 cm² area was found to be 32 ohm. Calculate κ and $\Lambda_{\rm eq.}$

Sol. Given
$$R = 32$$
 ohm, $l = 1.80$ cm, $a = 5.4$ cm²

$$\kappa = \frac{1}{R} \times \frac{l}{a} = \frac{1}{32} \times \frac{1.8}{5.4} = 0.01041 \,\text{S m}^{-1}$$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{0.01041 \times 1000}{0.1} = 104.1 \,\text{S cm}^2 \,\text{eq}^{-1}$$

ILLUSTRATION 3.73

 $\Lambda_{\rm eq}$ of 0.10 N solution of CaI₂ is 100.0 S cm² eq⁻¹ at 298 K. G^* of the cell = 0.25 cm⁻¹. How much current will flow when the potential difference between the electrode is 5 V?

Sol.
$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$
, $\kappa = \frac{\Lambda_{eq} \times N}{1000}$

$$= \frac{100 \times 0.1}{1000} = 0.01 \,\text{S cm}^{-1}$$

$$G(\text{conductance}) = \frac{K}{G^*(\text{cell constant})}$$

$$= \frac{0.01}{0.25} = 0.04 \,\text{ohm}^{-1} \,\text{or S}$$

$$R = \frac{1}{G} = \frac{1}{0.04} = 25 \,\text{ohm}$$

Current in ampere =
$$\frac{\text{Potential difference (by Ohm's law)}}{\text{Resistance (ohm)}}$$
$$= \frac{5}{25} = 0.2 \text{ A}$$

ILLUSTRATION 3.74

The resistance of a solution A is 50 ohm and that of solution B is 100 ohm, both solutions are taken in the same conductivity cell. If equal volumes of solution A and B are mixed, what is the resistance of the mixture using the same cell? (Assume there is no change or increase in the α of A and B on mixing)

Sol. For solution A.

Conductivity $(\kappa_A) = G$ (Conductance) $\times G^*$ (cell constant)

$$=\frac{1}{50}\times G^*$$
...(i)

For solution B,

Conductivity
$$(\kappa_B) = \frac{1}{100} \times G^*$$
 ...(ii) $\begin{pmatrix} \because G^* \text{ is same} \\ \text{for A and B} \end{pmatrix}$

When equal volumes of A and B are mixed, dilution becomes doubled in both the solutions. Hence, their individual contribution towards the conductivity of the mixture will be $\kappa_{\rm A}/2$ and $\kappa_{\rm B}/2$, respectively, and conductivity of the mixture

will be
$$\left(\frac{\kappa_{\rm A} + \kappa_{\rm B}}{2}\right)$$
.
For the mixture: $\left(\frac{\kappa_{\rm A} + \kappa_{\rm B}}{2}\right) = \frac{1}{R} \times G^*$...(iii)

$$R = 66.67$$
 ohm

3.16.7 IONIC CONDUCTANCE

The conductance of an ion in the solution is inversely proportional to its size in the aqueous solution. For example, Li^{\oplus} ion has a very high charge-to-size ratio (charge density) due to which it gets hydrated to a large extent, when dissolved in water.

Thus, Size of $Li^{\oplus}(aq) >>$ size of $Li^{\oplus}(g)$.

Note:

$$\begin{split} \bullet & \; r_{K^{\bigoplus}(g)} > r_{Na \bigoplus (g)} > r_{Li \bigoplus (g)} \; \text{but} \; r_{K^{\bigoplus}(aq)} < r_{Na \bigoplus (aq)} < r_{Li \bigoplus (aq)} \\ & \Rightarrow \; \Lambda_{m \; K^{\bigoplus}(aq)} > \Lambda_{m \; Na \bigoplus (aq)} > \Lambda_{m \; Li \bigoplus (aq)} \end{split}$$

- · A heavily hydrated ion drags water molecules along with it when it moves in a solution which makes it less mobile (or less conducting).
- Size of H[⊕](g) and ŎH (g) ions are extremely small yet they have a very high conductance value in the solution (as opposed to what you might have expected). In fact, H^{\oplus} ions have the highest Λ_{m} at any temperature followed by $\overset{\ominus}{\mathbf{O}}\mathbf{H}$ ions. The is due to the mechanism by which they travel in the aqueous solution.

H[⊕] moves in the solution as shown:

ILLUSTRATION 3.75

Arrange the following compounds in the order of increasing conductance in aqueous solution HCl, LiCl, NaCl, KCl.

Sol. Note that anion Cl[©] is same in all the given compounds. So, the conductance value will only depend on the size of cation in aqueous solution.

Since
$$\Lambda_{\text{m H}} > \Lambda_{\text{m K}} > \Lambda_{\text{m Na}} > \Lambda_{\text{m Li}}$$

Hence, $\Lambda_{\text{m HCl}} > \Lambda_{\text{m KCl}} > \Lambda_{\text{m NaCl}} > \Lambda_{\text{m LiCl}}$

ILLUSTRATION 3.76

Arrange the following compounds in the order of decreasing molar conductivity in aqueous solution.

i. a.
$$K[Co(NH_3)_2(NO_2)_4]$$

b.
$$[Cr(NH_3)_3(NO_2)_3]$$

c.
$$[Cr(NH_3)_5(NO_2)]_3 [Co(NO_2)_6]_2$$

d.
$$Mg[Cr(NH_3)(NO_2)_5]$$

ii. a. Li[Co(NH₃)₂ (NO₂)₄]

c. K[Co(NH₃)₂ (NO₂)₄]

iii. a. Pt(NH₃)₆ Cl₄ c. Co(NH3)4Cl3 **b.** Na[Co(NH₃)₂(NO₂)₄]

d. Cs[Co(NH₃)₂(NO₃)₄]

b. Cr(NH₃)₆Cl₂ d. K, PtCl

Sol. Conductance or conductivity in an aqueous solution depends on:

- Greater the number of ions in solution, more i_{S} the conductance.
- For same number of ions, greater the charge on the ion more is the conductance.
- If the number of ions and charge on the ions are equal then conductance is inversely proportional to its Size in the aqueous solution.

For example, the size of $Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$ Thus, smallest ion should move more rapidly, however ionic mobility shows the reverse trend because smaller ions are more extensively hydrated (due to high charge density) and thus hydrated ion size for these ions is:

$$\begin{array}{c} \text{Li}^{\oplus}(aq) > \text{Na}^{\oplus}(aq) > \text{K}^{\oplus}(aq) > \text{Rb}^{\oplus}(aq) > \text{Cs}^{\oplus}(aq) \\ \text{i. a. } \overset{\oplus}{\text{K}} \begin{bmatrix} +3 & 0 & -1 \times 4 \\ \text{Co}(\text{NH}_3)_2 & (\text{NO}_2)_4 \end{bmatrix} + \text{aq} & \Longrightarrow \end{array}$$

 $K^{\oplus} + [Co(NH_3), (NO_3)] =$ (Two ions with charge +1 or -1)

b.
$$\begin{bmatrix} +3 & 0 & -1 \times 3 \\ Cr(NH_3)_2 & (NO_2)_3 \end{bmatrix} + aq \rightleftharpoons$$

No ionization (no ions with zero charge

c.
$$\left[\overset{+3}{\text{Cr}} \overset{0}{(\text{NH}_3)_5} \overset{-1}{(\text{NO}_2)} \right]_3 \left[\overset{+3}{\text{Co}} \overset{-1 \times 6}{(\text{NO}_2)_6} \right]_2 + \dot{\text{aq}} \rightleftharpoons 3 \left[\overset{+3}{\text{Cr}} \overset{0}{(\text{NH}_3)_5} \overset{-1}{(\text{NO}_2)} \right]_2^{2+} + 2 \left[\overset{+3}{\text{Co}} \overset{-1 \times 6}{(\text{NO}_2)_6} \right]_2^{2+}$$

(Five ions with charge = +6 or -6

d.
$$Mg^{+2} \begin{bmatrix} +3 & 0 & -l \times 5 \\ Cr(NH_3)_5(NO_2)_5 \end{bmatrix}^{2-} + aq \Longrightarrow Mg^{2+} + \begin{bmatrix} +3 & 0 & -l \times 5 \\ Cr(NH_3)_5(NO_2)_5 \end{bmatrix}^{2-}$$

[Two ions with charge = +2 or -2So the decreasing order of conductance is:

ii. Since the anion part is same in all the coordination compounds and the number of ions produced in solution (2 ions) and charge (+1 or -1) is also same, so the conductance will depend on the size of the ions in aqueous medium and inversely proportional to its size. So, the size of these ions in aqueous solution is $Li^{\oplus}(aq) > Na^{\oplus}(aq) > K^{\oplus}(aq) > Cs^{\oplus}(aq)$ and conductance is reversed.

... Decreasing order of conductance is d > c > b > a

iii. In this question, first write these compounds in the form of coordinate of coordination compounds, knowing their coordination number. For example,

$$CN \text{ for } Pt^{4+}, Cr^{3+}, Co^{3+} = 6.$$

a.
$$Pt(NH_3)_6Cl_4 = [Pt(NH_3)_6]Cl_4 + aq \rightleftharpoons$$

$$\begin{bmatrix} +4 & 0 \\ Pt(NH_3)_6 \end{bmatrix}^{4+} + 4Cl^{\circ}$$

[5 ions with charge =
$$+4$$
 or -4]

b.
$$Cr(NH_3)_6Cl_3 = [Cr(NH_3)_6]Cl_3 + aq$$

$$\begin{bmatrix} +3 & 0 \\ Cr(NH_3)_6 \end{bmatrix}^{3+} + 3C1^{\odot}$$

[4 ions with charge = +3 or -3]

c.
$$Co(NH_3)_4Cl_3 = [Cr(NH_3)_4Cl_2]Cl \rightleftharpoons$$

(because $CN = 6$)

$$\begin{bmatrix} +3 & 0 & -1 \times 2 \\ \operatorname{Cr}(\operatorname{NH}_3)_4 & \operatorname{Cl}_2 \end{bmatrix}^{\oplus} + \operatorname{Cl}^{\odot}$$

(2 ions with charge = +1 or -1)

d.
$$K_2 PtCl_6 = K_2 [PtCl_6] + aq \implies 2K^{\oplus} + \begin{bmatrix} +4 & -1 \times 6 \\ Pt & Cl_6 \end{bmatrix}^{2-}$$
[3 ions with charge = +2 or -2]

So decreasing order of conductance is:

3.16.8 VARIATION OF SPECIFIC CONDUCTIVITY, EQUIVALENT, AND MOLAR CONDUCTIVITIES WITH CONCENTRATION

For both weak and strong electrolytes, the electrolytic conductance (G) as well as the equivalent conductivity (Λ_{eq}) and molar conductivity (Λ_{m}) increase with dilution whereas the specific conductivity (or conductivity) (κ) of an electrolytic solution decreases with dilution. This is explained as below.

The conductance of an electrolytic solution is due to the presence of ions in the solution. The greater is the number of ions, the greater is the conductance.

On dilution, more ions are produced in solution, so the conductance (G) also increases on dilution or decreases on increasing the concentration of the solution.

Conductivity (or specific conductivity, κ) always decreases with dilution, both for weak and strong electrolytes [Fig. 3.20(b)]. This is due to the fact that the total number of ions in the solution increases on dilution but the number of ions per unit volume that carry the current in the solution decreases on dilution. The specific conductivity (or conductivity, κ) of a solution at any given concentration is the conductance of one unit volume of solution kept between two electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation

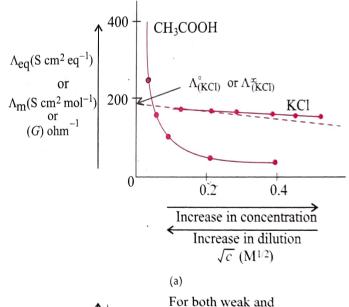
$$G = \frac{\kappa \times a}{l}$$
 [both l and a are unity in m or cm]

Equivalent conductivity (Λ_{eq}) and molar conductivity (Λ_{m}) of a solution at a given concentration is the conductance (G) of the volume V of a solution containing one gEq or one mole of electrolyte, respectively, kept between two electrodes with area of cross section a and distance of unit length.

Since l = 1 and a = V (volume containing 1 g equivalent or 1 mole of electrolyte)

$$\therefore \quad \Lambda_{\text{eq}} = \Lambda_{\text{m}} = \kappa \times V$$

Equivalent and molar conductivity increase on dilution (or decrease in concentration) because the total volume V of a solution containing 1 g equivalent or 1 mole of electrolyte also increases. It may be noted that decrease in k on dilution of a solution is more than compensated by increase in its volume. Physically, it means that at a given concentration, Λ_{ea} or Λ_{m} can be defined as the conductance (G) of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having the area of cross section large enough to accommodate sufficient volume of solution that contains 1 g equivalent or 1 mole of the electrolyte. When the concentration approaches zero (or infinite dilution), the equivalent or molar conductivity at infinite dilution is known as limiting equivalent or molar conductivity and is represented by the symbol $\Lambda_{\text{eq}}^{\circ}$ or $\Lambda_{\text{m}}^{\circ}$ (or $\Lambda_{\text{eq}}^{\infty}$ or $\Lambda_{\text{m}}^{\infty}$). The variation in Λ_{eq} or Λ_{m} with concentration (or dilution) is different for strong and weak electrolytes (Fig. 3.20).



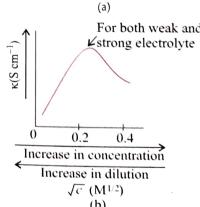


Fig. 3.20 (a) Molar conductivity $(\Lambda_{\rm m})$ or equivalent conductivity $(\Lambda_{\rm eq})$ or conductance (G) for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte, in aqueous solution). (b) Specific conductance (or conductivity) (κ) for strong and weak electrolytes in aqueous solution

Variation of $\Lambda_{\rm eq}$ or $\Lambda_{\rm m}$ with Dilution for Strong and Weak

Strong electrolytes

The Λ_{eq} or Λ_{m} of strong electrolyte increases slowly with dilution and can be represented by Debye Huckel-Onsager equation

$$\Lambda^{c}_{eq} = \Lambda^{\circ}_{eq} - A\sqrt{c} \text{ or } \Lambda^{c}_{eq} = \Lambda^{\infty}_{eq} - A\sqrt{c}$$

$$\Lambda^{c}_{m} = \Lambda^{\circ}_{m} - A\sqrt{c} \text{ or } \Lambda^{c}_{m} = \Lambda^{\infty}_{m} - A\sqrt{c}$$

If a plot of Λ_{eq} or Λ_{m} against \sqrt{c} is plotted [Fig. 3.20(a)], a straight line with intercept equal to Λ_{eq}° or Λ_{m}° and a slope equal to -A is obtained at lower concentration, but it is not linear for higher concentration. The value of the constant A for a given solvent and temperature depends on the type of electrolytes, i.e., the charges on the cation and anion produced during the dissociation of the electrolyte in the solution.

Thus, NaCl (Na[⊕] Cl[⊙]) is known as uni-univalent (or +1, -1) electrolyte

BaCl₂ (BaCl₂) is known as bi-univalent (or +2, -1) electrolyte.

CaSO₄ (CaSO₄) is known as bi-bivalent (or +2, -2)

Therefore, electrolytes of a particular type have the same value of A. For example, for $CaSO_4$ and $MgSO_4$ (+2, -2 type), the value

Moreover, the curve obtained for a strong electrolyte shows that there is small increase in G, Λ_{eq} , or Λ_{m} with dilution. This is because a strong electrolyte is completely ionized in solution and so the number of ions remains almost constant.

At higher concentration, the greater inter-ionic interaction decreases the movement of the ions and therefore conductance decreases with increasing concentration.

On dilution, the ions are far apart, and therefore interionic attraction decreases and hence conductance increases and approaches a maximum limiting value at infinite dilution.

Weak electrolytes

The conductance of weak electrolytes is less than that of strong electrolytes at the same concentration since weak electrolytes are not completely ionized [Fig. 3.20(a)].

Moreover, the curve for weak electrolytes shows that there is a very large increase in the conductance with dilution near the infinite dilution since on dilution the degree of ionization increases. Thus, an increase in conductance with dilution is due to the increase in the number of ions in the solution. However, it does not reach a limiting value.

It is also observed that the plot for a strong electrolyte becomes linear near high dilution and can be extrapolated to zero concentration to get the value of Λ°_{m} or Λ°_{eq} .

However, for a weak electrolyte, $\Lambda_{\rm m}$ or $\Lambda_{\rm eq}$ increases sharply near high dilution. Hence, an extrapolation at infinite dilution is not possible [Fig. 3.20(a)]. Experimentally, it is also not possible to determine the Λ°_{eq} or Λ°_{m} value for a weak electrolyte because although the ionization is complete but the number of ions per unit volume is so low that the conductivity cannot be measured

This problem was solved by Kohlrausch who gave a law known as Kohlrausch law.

3.17 KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

Kohlrausch concluded that each ion makes a definite contribution to the total molar conductivity of an electrolyte at infinite dilution irrespective of the nature of the other ion of the electrolyte. This individual contribution of an ion towards the total molar conductiv. ity of the electrolyte is called *molar ionic conductivity*. As a result of these studies Kohlrausch in 1876 put forward a generalization known after him as Kohlrausch law. It states as under:

The molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and anions each multiplied with the number of ions present in one formula unit of the electrolyte.

Mathematically,

$$\Lambda^{\circ}_{m}$$
 for $A_{x}B_{y} = x\lambda^{\circ}_{Ay^{+}} + y\lambda^{\circ}_{B^{x-}}$

where Λ°_{m} is the limiting molar conductivity of the electrolyte at infinite dilution.

 $x\lambda^{\circ}A^{\oplus}$ and $y\lambda^{\circ}B^{\ominus}$ are the limiting molar conductivities of the cations and anions, respectively, at infinite dilution.

For example,

$$\Lambda_{m}^{\circ}$$
 for NaCl = $\lambda_{Na}^{\circ} + \lambda_{Cl}^{\circ}$
 Λ_{m}° for BaCl₂ = $\lambda_{Ba}^{\circ} + 2\lambda_{Cl}^{\circ}$
 Λ_{m}° for Al₂(SO₄)₃ = $2\lambda_{Al}^{\circ} + 3\lambda_{SO}^{\circ}$

In terms of equivalent conductivities, Kohlrausch's law is defined as:

The equivalent conductivity of an electrolyte at infinite dilution is the sum of two values one depending upon the cation and the other upon the anion, i.e.,

$$\Lambda^{\circ}_{eq} = \lambda^{\circ}_{c} + \lambda^{\circ}_{a}$$

where Λ°_{eq} is the limiting equivalent (or ionic) conductivity of the electrolyte, and $\lambda^\circ_{\ c}$ and $\lambda^\circ_{\ a}$ are the limiting equivalent (or ionic conductivities of the cation and anion, respectively, at infinite dilution. Kohlrausch examined $\Lambda_{\rm m}^{\circ}$ values for a number of small electrolytes and observed certain regularities. It was found that the difference in Λ_{m}° of the electrolytes NaX and KX for any X is nearly constant. For example,

$$\begin{split} \Lambda^{\circ}_{m(KCI)} - \Lambda^{\circ}_{m(NaCI)} &= \Lambda^{\circ}_{m(KBr)} - \Lambda^{\circ}_{m(NaBr)} \\ \text{or} &= \Lambda^{\circ}_{m(KI)} - \Lambda^{\circ}_{m(NaI)} \approx 23.4 \text{ S cm}^2 \text{ mol}^{-1} \\ \begin{bmatrix} \lambda^{\circ}_{K^{\oplus}} + \lambda^{\circ}_{CI^{\odot}} - \lambda^{\circ}_{Na^{\oplus}} - \lambda^{\circ}_{CI^{\odot}} = \lambda^{\circ}_{K^{\oplus}} - \lambda^{\circ}_{Br^{\odot}} - \lambda^{\circ}_{Na^{\oplus}} - \lambda^{\circ}_{Br^{\odot}} \\ &= \lambda^{\circ}_{K^{\oplus}} + \lambda^{\circ}_{I^{\odot}} - \lambda^{\circ}_{Na^{\oplus}} - \lambda^{\circ}_{I^{\odot}} \\ &\approx 23.4 \text{ S cm}^2 \text{ mol}^{-1} \end{split}$$

and similarly it was found that $\Lambda^{\circ}_{m(NaBr)} - \Lambda^{\circ}_{m(NaCl)} = \Lambda^{\circ}_{m(KBr)} - \Lambda^{\circ}_{m(KCl)} \approx 1.8 \, \text{S cm}^2 \, \text{mpc}^{-1}$ or $\left[\lambda^{\circ}_{N_{a}^{\oplus}} + \lambda^{\circ}_{Br^{\ominus}} - \lambda^{\circ}_{N_{a}^{\oplus}} - \lambda^{\circ}_{Cl^{\ominus}} = \lambda^{\circ}_{K^{\oplus}} + \lambda^{\circ}_{Br^{\ominus}} - \lambda^{\circ}_{K^{\oplus}} - \lambda^{\circ}_{Cl^{\ominus}}\right]$

3.17.1 APPLICATIONS OF KOHLRAUSCH LAW

$_{\mbox{\it Calculation}}$ of Molar Conductivity and Equivalent $_{\mbox{\it Conductivity}}$ at Infinite Dilution (Λ° or Λ^{∞}) for Weak $_{\mbox{\it Electrolyte}}$

Molar or equivalent conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally or by plotting a graph. This is because the conductance of such electrolyte is low and dissociation of such an electrolyte is not complete even at infinite dilution. Therefore, using Kohlrausch law of independent migration of ions, it is possible to calculate Λ°_{m} or Λ°_{eq} for any electrolyte from Λ° of individual ions. For example, for weak electrolytes such as acetic acid, it is possible to determine Λ°_{m} or Λ°_{eq} as

$$\Lambda^{\circ}_{m (CH_3COOH)} = \lambda^{\circ}_{CH_3COO} + \lambda^{\circ}_{H} \oplus$$

This equation can be obtained by knowing the molar or equivalent conductivities at infinite dilution for the strong electrolytes such as KCl, CH₃COOK, and HCl, as by Kohlrausch law.

$$\begin{split} & \Lambda^{\circ}_{m(CH_{3}COOK)} = \lambda^{\circ}_{CH_{3}COO\odot} + \lambda^{\circ}_{K} \oplus \\ & \lambda^{\circ}_{m(KCl)} = \lambda^{\circ}_{K} \oplus + \lambda_{Cl} \ominus \\ & \lambda^{\circ}_{m(HCl)} = \lambda^{\circ}_{H} \oplus + \lambda_{Cl} \ominus \end{split}$$

Thus,

$$\begin{split} & \Lambda^{\circ}_{m(\text{CH}_3\text{COOH})} = \Lambda^{\circ}_{m(\text{CH}_3\text{COOK})} + \Lambda^{\circ}_{m(\text{HCl})} - \Lambda^{\circ}_{m(\text{KCl})} \\ \text{or} & [\lambda^{\circ}_{\text{CH}_3\text{COO}\ominus} + \lambda^{\circ}_{\text{H}\oplus}] = [\lambda^{\circ}_{\text{CH}_3\text{COO}\ominus} + \lambda^{\circ}_{\text{K}\oplus}] + [\lambda^{\circ}_{\text{H}\oplus} + \lambda^{\circ}_{\text{Cl}\ominus}] \\ & \qquad \qquad - [\lambda^{\circ}_{\text{K}\oplus} + \lambda^{\circ}_{\text{Cl}\ominus}] \end{split}$$

Calculation of the Degree of Dissociation

According to Arrhenius theory of electrolytic dissociation, on dilution, the degree of ionization increases and at infinite dilution the dissociation is almost complete. So on dilution increasing the number of ions increases the molar conductivity and is maximum at infinite dilution. Thus, if $\lambda^c_{\ m}$ or $\lambda^c_{\ eq}$ is the molar or equivalent conductivity of a solution at any concentration c, and $\Lambda^\circ_{\ m}$ or $\Lambda^\circ_{\ eq}$ is the molar or equivalent conductivity at infinite dilution, then, for weak electrolytes,

Degree of dissociation (
$$\alpha$$
) = $\frac{\Lambda_{m}^{c}}{\Lambda_{m}^{o}} = \frac{\Lambda_{eq}^{c}}{\Lambda_{eq}^{o}}$

The value of Λ°_{m} or Λ°_{eq} for a weak electrolyte is calculated using Kohlrausch law.

Calculation of the Dissociation Constant of a Weak Electrolyte (K_a or K_b)

For weak electrolytes such as CH_3COOH or NH_4OH , it is possible to determine the value of its dissociation constant, if the value of α is known. Thus,

$$K_{\rm a} = \frac{c\alpha^2}{(1-\alpha)} = \frac{c(\Lambda_{\rm m}^c)^2}{(\Lambda_{\rm m}^o)^2 \left(1 - \frac{\Lambda_{\rm m}^c}{\Lambda_{\rm m}^o}\right)} = \frac{c(\Lambda_{\rm m}^c)^2}{\Lambda_{\rm m}^o(\Lambda_{\rm m}^o - \Lambda_{\rm m}^c)}$$

Calculation of the Solubility of Sparingly Soluble Salt

If a solute is sparingly soluble in a given solvent, its concentration is taken as its solubility in the saturated solution.

Moreover, the given salt is very less soluble in the given solvent. Its molar or equivalent conductivity at some concentration is taken as its molar or equivalent conductivity at infinite dilution.

Thus,
$$\lim_{c\to 0} \Lambda_{m}^{c} = \Lambda_{m}^{\circ}$$
 and $\lim_{c\to 0} \Lambda_{eq}^{c} = \Lambda_{eq}^{\circ}$

Thus,
$$\lim_{c\to 0} \Lambda_{m}^{c} = \Lambda_{m}^{o} = \frac{\kappa \times 1000}{M}$$
 or $\frac{\kappa \times 1000}{S}$

$$(S = \text{solubility in mol } L^{-1})$$

$$\lim_{c \to 0} \Lambda^{c}_{eq} = \Lambda^{o}_{eq} = \frac{\kappa \times 1000}{N} \text{ or } \frac{\kappa \times 1000}{S}$$

$$(S = \text{solubility in Eq L}^{-1})$$

 Λ°_{m} or Λ°_{eq} can be computed using Kohlrausch law.

Thus, S can be computed and can be used to calculate the solubility product. For example, for $Al(OH)_3$, if S mol L^{-1} is the solubility, then

Al(OH)₃
$$\rightleftharpoons$$
 Al³⁺ + 3 $\stackrel{\odot}{O}$ H
 S 3S
 $K_{sp} = [Al^{3+}] \stackrel{\odot}{[OH]}^3 = S \times (3S)^3 = 27S^4$

ILLUSTRATION 3.77

The conductivity (κ) of a saturated solution of AgBr at 298K is 8.5×10^{-7} S cm⁻¹. If λ°_{Ag} and λ°_{Br} are 62 and 78 S cm⁻² mol⁻¹, respectively, then calculate the solubility and K_{sp} of AgBr.

Sol.
$$\Lambda^{\circ}_{m(AgBr)} = \lambda^{\circ}_{Ag} + \lambda^{\circ}_{Br}$$

$$= 62 + 78 = 140.0 \text{ S cm}^{2} \text{ mol}^{-1}$$

$$\therefore \Lambda^{\circ}_{m(AgBr)} = \Lambda_{m(AgBr)} = \frac{\kappa \times 1000}{S}$$

$$140.0 \text{ S cm}^{2} \text{ mol}^{-1} = \frac{8.5 \times 10^{-7} \times 10^{3}}{S}$$

$$S = 8.5 \times 10^{-7} \times 10^{3}/140.0$$

$$= 0.06 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 0.06 \times 10^{-4} \times Mw_{\text{(AgBr)}}$$

$$= 0.06 \times 10^{-4} \times 188 \text{ g L}^{-1}$$

$$= 1.128 \times 10^{-3} \text{ g L}^{-1}$$

$$\therefore K_{\text{sp}} \text{ of AgBr} = S^{2} M^{2} = (0.06 \times 10^{-4})^{2}$$

$$= 3.6 \times 10^{-11} \text{ mol}^{2}\text{L}^{-2}$$

ILLUSTRATION 3.78

The conductivity of 0.001028 M acetic acid is 4.95×10^{-5} S cm⁻¹. Calculate dissociation constant if Λ_m° for acetic acid is 390.5 S cm² mol⁻¹.

Sol.
$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 48.15 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_{\text{m}}^{c}}{\Lambda_{\text{m}}^{\circ}} = \frac{48.15 \text{ S cm}^{2} \text{ mol}^{-1}}{390.5 \text{ S cm}^{2} \text{ mol}^{-1}} = 0.1233$$

$$K_{\rm a} = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \,\text{mol L}^{-1} \times (0.1233)^2}{(1-0.1233)}$$

$$= 1.78 \times 10^{-5} \text{ mol L}^{-1}$$

ILLUSTRATION 3.79

The molar conductivity of acetic acid at infinite dilution is 390.7 and for 0.01 M acetic acid is 3.907 S cm² mol⁻¹. Calculate (a) α and (b) pH of solution.

Sol.
$$\alpha = \frac{\Lambda_{m}^{c}}{\Lambda_{m}^{\circ}} = \frac{3.907}{390.7} = 0.01$$

$$CH_3COOH \rightleftharpoons CH_3COO^{\odot} + H^{\oplus}$$

Initial conc

Final conc

$$c(1-\alpha)$$

$$\therefore [H^{\oplus}] = c\alpha = 0.01 \times 0.01 = 10^{-4} \text{ M}$$

$$pH = -log(10^{-4}) = 4$$

ILLUSTRATION 3.80

The ionic equivalent conductivities of $C_2O_4^{\ 2-}$, K^\oplus , and Na^\oplus ions are x, y, and $z \ S \ cm^2 \ Eq^{-1}$ respectively. Calculate Λ_{eq}° of (NaOOC—COOK).2H₂O.

Sol. Total charge = 2

Number of equivalent of ion = $\frac{\text{Charge on the ions}}{\text{Total charge}}$

$$\therefore \text{ Equivalent of C}_2 O_4^{2-} = \frac{2}{2} = 1$$

Equivalent of Na^{$$\oplus$$} = $\frac{1}{2}$, Eq of K ^{\oplus} = $\frac{1}{2}$

$$\therefore \Lambda_{\text{eq (NaOOC}-\text{COOK)}}^{\circ} = \lambda_{\text{eq(C}_2\text{O}_4^{2-})}^{\circ} + \frac{1}{2} \lambda_{\text{eq (Na}^{\oplus})}^{\circ} + \frac{1}{2} \lambda_{\text{eq(K}^{\oplus})}^{\circ}$$

$$= \left(x + \frac{y}{2} + \frac{z}{2}\right) \operatorname{S} \operatorname{cm}^{2} \operatorname{eq}^{-1}$$

ILLUSTRATION 3.81

The ionic molar conductivities of $C_2O_4^{2-}$, K^\oplus , and Na^\oplus io_{NS} a_{re} x', y', and z' S cm² mol⁻¹, respectively. Calculate Λ_m° and Λ_{cq}° of (NaOOC—COOK).2H₂O.

Sol.
$$\Lambda_{m}^{\circ} = \lambda_{m(C_{2}O_{4}^{2-})}^{\circ} + \lambda_{m(Na\oplus)}^{\circ} + \lambda_{m(K\oplus)}^{\circ}$$

$$= (x' + y' + z') \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{\text{eq}}^{\circ} = \frac{\Lambda_{\text{m}}^{\circ}}{\text{Total charge}} = \frac{(x' + y' + z')}{2} \text{ S cm}^2 \text{ Eq}^{-1}$$

Comparing the solution with that of illustration 3.80, we get

$$\left(x + \frac{y}{2} + \frac{z}{2}\right) = \left(\frac{x' + y' + z'}{2}\right)$$

ILLUSTRATION 3.82

The ionic equivalent conductivities of K^{\oplus} , Al^{3+} , and SO_4^{2-} ions are x, y, and z S cm² Eq⁻¹ and ionic molar conductivities are x', y', z' respectively. Calculate Λ°_{m} and Λ°_{eq} for $(K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O)$ (Potash alum).

Sol.
$$\Lambda^{\circ}_{m}$$
 for potash alum = $2\lambda^{\circ}_{m(K^{\oplus})} + 2\lambda^{\circ}_{m(Al^{3+})} + 4\lambda^{\circ}_{m(SO_{2}^{2-})}$

$$= (2x' + 2y' + 4z') \text{ S cm}^2 \text{ mol}^{-1}$$

Total charge on potash alum = (+8 or -8)

Number of equivalent of ion = $\frac{\text{Charge on the ions}}{\text{Total charge}}$

$$\Lambda_{\text{eq}}^{\circ} = \left(\frac{2x' + 2y' + 4z'}{8}\right)$$

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \longrightarrow 2K^{\oplus} + 2Al^{3+} + 4SO_4^{2-}$$

$$+24H_{2}$$

...(i)

$$\therefore$$
 Equivalent of $K^{\oplus} = \frac{+1 \times 2}{+8} = \frac{1}{4}$ Eq

$$\therefore \text{ Equivalent of Al}^{3+} = \frac{+3 \times 2}{+8} = \frac{3}{4} \text{ Eq}$$

$$\therefore \text{ Equivalent of SO}_4^{2-} = \frac{-2 \times 4}{-8} = 1 \text{ Eq}$$

$$\Lambda_{eq(potash\; alum)}^{o} = \lambda_{eq(K^{\bigoplus})}^{o} + \lambda_{eq(Al^{3^{+}})}^{o} + \lambda_{eq(SO_{4}^{2^{-}})}^{o}$$

$$= \frac{1}{4} \times x + \frac{3}{4} \times y + 1 \times z = \left(\frac{x}{4} + \frac{3y}{4} + z\right) \qquad ...(ii)$$

Comparing equivalent conductivities (i) and (ii)

$$\left(\frac{x}{4} + \frac{3y}{4} + z\right) \text{S cm}^2 \text{ Eq}^{-1} = \left(\frac{2x' + 2y' + 4z'}{8}\right) \text{S cm}^2 \text{ Eq}^{-1}$$

ILLUSTRATION 3.83

From the following molar conductivities at infinite dilution:

$$\Lambda_{\text{m}}^{\circ}$$
 for Ba(OH)₂ = 457.6 Ω^{-1} cm² mol⁻¹

$$\Lambda_{\rm m}^{\circ}$$
 for BaCl₂ = 240.6 Ω^{-1} cm² mol⁻¹

$$\Lambda^{\circ}_{m}$$
 for NH₄Cl = 129.8 Ω^{-1} cm² mol⁻¹

Calculate Λ°_{m} for $NH_{4}OH$.

Sol. Refer section 3.17.2

$$\begin{split} \Lambda_{m\,[Ba(OH)_2]}^{\circ} &= \lambda_{Ba}^{\circ}{}_{2^{+}} + 2\lambda_{OH}^{\circ} = 457.6 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda_{m\,(BaCl_2)}^{\circ} &= \lambda_{Ba}^{\circ}{}_{2^{+}} + 2\lambda_{Cl}^{\circ}{}_{OH} = 240.6 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda_{m\,(NH_4Cl)}^{\circ} &= \lambda_{NH_4\oplus}^{\circ} + \lambda_{Cl}^{\circ}{}_{OH} = 129.8 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda_{m\,(NH_4OH)}^{\circ} &= \Lambda_{m(NH_4Cl)}^{\circ} + \frac{1}{2} \Lambda_{m\,[Ba(OH)_2]}^{\circ} - \frac{1}{2} \Lambda_{m\,(BaCl_2)}^{\circ} \\ &= 129.8 + \frac{1}{2} (457.6) - \frac{1}{2} (240.6) \end{split}$$

3.17.2 DETERMINATION OF IONIC PRODUCT OF WATER FROM CONDUCTANCE MEASUREMENT

 $= 238.3 \text{ S cm}^2 \text{ mol}^{-1}$

The ionic product of water is, $K_{\mathbf{w}} = [\mathbf{H}^{\oplus}] \stackrel{\odot}{[\mathrm{OH}]}$

Since in pure water, $[H^{\oplus}] = [OH] = 10^{-7} \text{ M}$,

$$\therefore \quad [\mathbf{H}^{\oplus}] = [\overset{\odot}{\mathbf{O}}\mathbf{H}] = \sqrt{K_w} \qquad \dots (\mathbf{i})$$

The ions are present in such low concentration that molar ionic conductivities may be taken as the ones at infinite dilution, so that:

$$\lambda_{H^{\oplus}} = \lambda^{\circ}_{H^{\oplus}} \text{ and } \lambda \overset{\odot}{O}H \approx \lambda^{\circ}\overset{\odot}{O}H$$
or $[\lambda^{\circ}_{H^{\oplus}} + \lambda^{\circ}\overset{\odot}{O}H = 547.6 \text{ S cm}^2 \text{ mol}^{-1}]$

$$\therefore \quad \Lambda_{eq}^{\circ} = \Lambda_{eq} \text{ (or } \Lambda_{m}^{\circ} = \Lambda_{m} \text{) for water.}$$

(Since total positive or negative charge = 1)

$$= \frac{\kappa \times 1000}{N}$$

$$\therefore N \text{ for H}_2 O = M \text{ for H}_2 O = \frac{\kappa \times 1000}{\Lambda_{\text{eq}}^{\circ} (\text{or } \Lambda_{\text{m}}^{\circ})}$$

$$H^{\mathfrak{S}} = [\overset{\circ}{O}H] = \frac{\kappa \times 1000}{\Lambda^{\circ}_{eq} (or \Lambda^{\circ}_{m})}$$

$$K_{W} = [H^{\oplus}][\tilde{O}H] = \left[\frac{\kappa \times 1000}{\Lambda_{eq}^{\circ} (\text{or } \Lambda_{m}^{\circ})}\right]^{2}$$

3.17.3 DETERMINATION OF HYDROLYSIS CONSTANT $(K_{\rm H})$ OF A SALT OF STRONG ACID AND WEAK BASE $(S_{\rm A}/W_{\rm B})$ FROM CONDUCTIVITY MEASUREMENT

 $K_{\rm h}$ of a salt can be determined from conductivity measurements. Let c be the concentration of the salt BH $^{\oplus}$ Cl $^{\ominus}$ (e.g., NH $_{4}$ $^{\oplus}$ Cl $^{\ominus}$) formed from a weak base (W $_{\rm B}$) and strong (S $_{\rm A}$). BH $^{\oplus}$ (cation of the salt) undergoes hydrolysis in the solution as:

$$BH^{\oplus} + H_2O \Longrightarrow B + H_3O^{\oplus}$$

If h is the degree of hydrolysis, then

$$[BH^{\oplus}] = c(1-h).$$
 $[H_3O^{\oplus}] = ch$

$$[Cl_{\Theta}] = [BH_{\Theta}] + [H^{3}O_{\Theta}]$$

Therefore, conductivity of the solution is given by

$$\kappa_1 = (1 - h)\kappa_2 + h\kappa_3 \qquad ...(i)$$

Rearranging equation (i), we get
$$h = \frac{\kappa_1 - \kappa_2}{\kappa_3 - \kappa_2}$$
 ...(ii)

where κ_2 is the conductivity of the unhydrolyzed salt of concentration c, and κ_3 is the conductivity of the HCl solution of concentration c. An alternate form of equation (i) is:

$$\Lambda_{m1} = (1 - h)\Lambda_{m2} + h\Lambda_{m3} \qquad ...(iii)$$

Rearranging equation (iii), we get

$$h = \Lambda_{m1} - \Lambda_{m2} / \Lambda_{m3} - \Lambda_{m2} \qquad ...(iv)$$

where $\Lambda_{\rm m1}$ is the molar conductivity of the hydrolyzed solution; $\Lambda_{\rm m2}$ is the molar conductivity of the unhydrolyzed solution of concentration c; and $\Lambda_{\rm m3}$ is the molar conductivity of the HCl solution of concentration c.

Note: The value of κ_2 or Λ_{m2} can be determined experimentally by adding an excess of the base to the solution, which causes equilibrium to shift to the left, i.e., it minimizes the hydrolysis.

Knowing the value of h from either of the two equations (i) to (iv), the hydrolysis constant (K_h) can be obtained by using the expression:

$$K_{\rm h} = \frac{ch^2}{1 - h}$$

ILLUSTRATION 3.84

An aqueous solution of 0.001 M aniline hydrochloride $^{\oplus}$ (Ph NH₃ Cl $^{\ominus}$) had $\Lambda_{\rm m}=120.0~{\rm S~cm^2~mol^{-1}}$. When few drops of a weak base (aniline, PhNH₂) is added, $\Lambda_{\rm m}$ decreases to 100.0 S cm 2 mol $^{-1}$. $\Lambda_{\rm m(HCl)}$ at same concentration = 400 S cm 2 mol $^{-1}$. Calculate h (degree of hydrolysis) and K_h

Sol. Aniline hydrochloride (Ph NH₃ Cl^{\odot}) is a salt of strong acid (HCl) and weak base (PhNH₂).

Using the expression (iii) and (iv) given is section (3.20.3),

$$\Lambda_{\text{m1(salt)}} = (1 - h)\Lambda_{\text{m2(salt + base)}} + h\Lambda_{\text{m3(HCl)}}$$

(hydrolysis constant) of aniline hydrochloride.

$$h = \frac{\Lambda_{m_1} - \Lambda_{m_2}}{\Lambda_{m_3} - \Lambda_{m_2}}$$
$$= \frac{(120 - 100)}{(400 - 100)} = \frac{20}{300} = 0.06$$

Now, KCl =
$$\frac{ch^2}{(1-h)} = \frac{(0.001 \text{ M}) (0.06)^2}{(1-0.06)}$$

= $3.8 \times 10^{-6} \text{ M}$

ILLUSTRATION 3.85

At 298 K, the conductivity of pure water is 5.476×10^{-8} S cm⁻¹.

The ionic conductances of H^{\oplus} and $\overset{\smile}{O}H$ at this temperature are 349.0 and 198.6 S cm² Eq⁻¹. Calculate K_W of water.

Sol.
$$\Lambda_{\text{eq}}^{\circ} = \lambda_{\text{H}}^{\circ} + \lambda_{\text{OH}}^{\circ} = (349.0 + 198.6)$$

$$= 547.6 \text{ S cm}^2 \text{ Eq}^{-1}$$

$$\therefore K_w = \left(\frac{\kappa \times 1000}{547.6 \text{ S cm}^2 \text{ mol}^{-1}}\right)^2$$

$$= \left(\frac{5.476 \times 10^{-8} \times 10^3}{547.6}\right)^2 = 10^{-14}$$

3.17.4 Abnormally High Conductivities of H^{\oplus} AND OH IONS

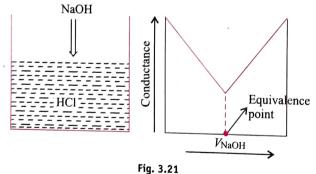
The molar conductivities of H^{\oplus} and $\stackrel{\mbox{\scriptsize old}}{O}H$ ions are much higher than those of other ions. Grothus explained it on the basis of a proton jump from one water molecule to another. This results in a more rapid transfer of positive charge from one region of the solution to another than would be possible if the ion $H_3\mathsf{O}^\oplus$ has to push its way through the solution as other ions do.

This also occurs in any other solvent. Thus, for example, in liquor NH_3 , the Λ_m of its characteristic cation or anion (namely $\widetilde{NH_4}$ and $\widetilde{NH_2}$) will have unusually high values than any other cations or anions.

3.18 CONDUCTOMETRIC TITRATION

The electrical conductivity of a solution serves as a means of determining the end point in a chemical reaction, involved in the titration of acids and bases or precipitation. The measurement of conductance of resulting solution from an acid and base titration is used to calculate equivalence point if there is a regular change in the conductance and sharp change at equivalence point.

a. Strong acid (HCl) vs strong base (NaOH) (S_A/S_D)



The conductivity of NaOH is due to Na[®] and OH ions, whereas that of HCl is due to H[⊕] and Cl[⊙] ions. When a drop of NaOH is added to a certain volume of HCl solution taken in a conductivity cell, NaOH reacts with equivalent amount of HCl.

$$NaOH + HCl \longrightarrow Na^{\oplus} Cl^{\ominus} + H_2O$$

Before NaOH is added, the conductance of HCl has a high value due to the presence of highly mobile H^{\oplus} ions.

As NaOH is added, H[®] ions combine with $^{\circ}_{OH}$ ions faster may: As NaOH is accepted H_2O , and thus faster moving H_2O to form undissociated H_2O , and thus faster moving H_2O Consequently, the conductance of the solution decreases and this continues right up to the equivalence point, if more of NaOH is added. Then, the solution contains an $exce_{SS of}$ fast moving OH ions. With the result that its conductance is increased and continues to increase as more and more of NaOH is added.

b. Strong acid (HCl) vs weak base (NH₄OH) (S_A/W_D)

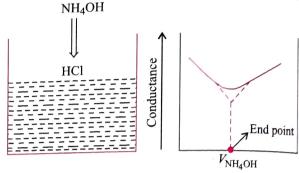


Fig. 3.22

In this case, there is a replacement of fast moving H[®] ions by slow moving NH_4^{\oplus} ions as the following reaction proceeds:

$$H^{\oplus}Cl^{\ominus} + NH_4^{\oplus}OH \longrightarrow NH_4^{\oplus}Cl^{\ominus} + H_2O$$

Consequently a fall in conductivity is observed to the end point. After the equivalence point the conductivity remains practically constant because NH4OH has very low conductivity as compared to HCl or NH4Cl. A slight curvature is noticed near the end point. This is explained on the basis of the following reaction taking place simultaneously:

$$NH_4^{\oplus} + 2H_2O \Longrightarrow NH_4OH + H_3O^{\oplus}$$

This reaction results in the generation of fast moving H₃0° ions. It is due to the H_3O^{\oplus} ions produced by hydrolysis in the system that the fall in the conductivity of the solution is arrested and a curvature in the plot is observed.

c. Titration curve of W_A/S_B (CH₃COOH vs NaOH)

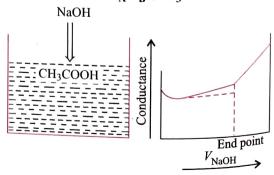


Fig. 3.23

Before the addition of NaOH, the solution shows poor conductance described by the solution shows poor conductance due to feeble ionization of CH₃COOH. Initially the addition of CH₃COOH. the addition of NaOH causes not only the replacement of H

by Na^{\oplus} but also suppresses the dissociation of acetic acid due to common ion Ac^{\ominus} , and thus the conductance of the solution decreases in the beginning. But soon the conductance starts increasing as the addition of NaOH neutralizes the undissociated HAc to $Na^{\oplus}Ac^{\ominus}$, thus causing the replacement of non-conducting HAc with strong conducting $Na^{\oplus}Ac^{\ominus}$. This continues upto equivalence point. Beyond this point, conductance increases more rapidly with the addition of NaOH due to high-conducting OH ions.

The graph near the equivalence point is curved due to the hydrolysis of salt NaAc.

d. Titration curve of strong acid (HCl) vs weak base (NH₄OH) (S_A/W_B)

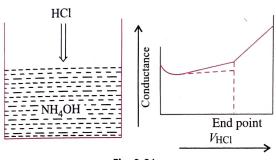


Fig. 3.24

Follow similar discussion as in point (c).

e. Titration curve of weak acid (CH $_3$ COOH) vs weak base (NH $_4$ OH) (W $_A$ /W $_B$)

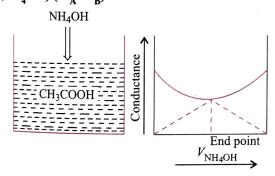


Fig. 3.25

The nature of the curve before the equivalence point is similar to that in (c). After the equivalence point, conductance virtually remains the same as weak base which is being added is feebly ionized and therefore is not fairly conducting.

f. Titration curve of the mixture of weak and strong acids (HCl + CH₃COOH) against a strong base (NaOH)

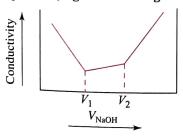


Fig. 3.26(a)

In this case, S_A is first neutralized after that W_A starts neutralizing. Thus, we have the neutralization reaction in two stages and the curve contains two breaks as shown in Fig. 3.27.

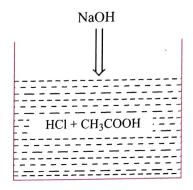


Fig. 3.26(b)

g. Besides the above titrations, the titration involving a mixture of weak and strong bases (NaOH + NH₄OH vs HCl), oxalic acid vs NaOH (stepwise neutralization) (two breaks in the curve), precipitation (NaCl vs. AgNO₃), oxidation reduction (Fe²⁺ vs MnO₄ $^{\odot}$), displacement reactions (NaAc vs HCl) and other types of reactions can be studied.

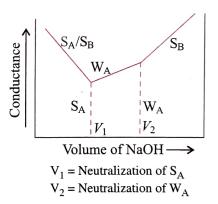


Fig. 3.27

This method is very important where a direct titration using indicators is either difficult or impossible. The conductometric titrations curve given in Figs. 3.21–3.27 are actually observed only if the volume of the solution remains unchanged. This condition is fulfilled by taking the solution in the burette about 10–20 times more concentrated than the solution in the titrating flask.

CONCEPT APPLICATION EXERCISE 3.3

- 1. The conductivity (κ) of a saturated solution of AgBr at 298K is 8.5×10^{-7} S cm⁻¹. If $\lambda^{\circ}_{Ag\oplus}$ and $\lambda^{\circ}_{Br\odot}$ are 62 and 78 S cm² mol⁻¹, respectively, then calculate the solubility and $K_{\rm sp}$ of AgBr.
- 2. At 25°C, $\lambda_{\rm m(H^{\oplus})}^{\circ} = 3.50 \times 10^{-2} \ \rm ohm^{-1} \ m^2 \ mol^{-1}$ and $\lambda_{\rm m(OH)}^{\circ} = 2.0 \times 10^{-2} \ \rm ohm^{-1} \ m^2 \ mol^{-1}$. If the conductivity of pure water is $5.7 \times 10^{-6} \ \rm ohm^{-1} \ m^{-1}$, determine $K_{\rm w}$ (ionic product) of water. (Density of H₂O = 1 g mL⁻¹)

- 3. At 298 K, Λ°_{eq} of propanoic acid is 386.6 S cm² eq⁻¹. If its ionization constant (K_a) is 1.4×10^{-5} . Calculate Λ_{eq} of 0.05 N propanoic acid at 298 K.
- 4. The conductivity of $\rm H_2O$ in a big irregular-shaped vessel contained water whose conductivity is 2.0×10^{-5} S cm⁻¹. 585 g of NaCl was then added to the water and the conductivity after the addition of NaCl is 3.0×10^{-5} S cm⁻¹. Find the capacity of the vessel if it is fulfilled with water. Given: $\Lambda_{\rm m(NaCl)}^{\circ} = 150.0$ S cm² mol⁻¹.
- 5. $\Lambda^{\circ}_{\text{m(AgNO_3)}}$, $\Lambda^{\circ}_{\text{m(HCl)}}$, and $\Lambda^{\circ}_{\text{m(HNO_3)}}$ are a, b, and $c \text{ S cm}^2$ mol⁻¹, respectively. If the conductivity of saturated AgCl solution is $z \text{ S cm}^{-1}$. Calculate the K_{sp} of AgCl.
- 6. A hydrogen electrode and a calomel half cell are used to determine the pH of a solution on a mountain top where the pressure is 500 mm of Hg. The pressure was wrongly assumed to be 760 mm of Hg and pH was found to be 4. What is the correct pH?

The cell is $H_2(g)$ | solution || KCl, Hg_2Cl_2 | Hg.

7. At 25°C, after the addition of 110 mL of 0.1 N NaCl solution to 100 mL of 0.1 N AgNO₃ solution, the reduction potential of a silver electrode placed in it is 0.36 V. Assuming activities to be identical with concentrations, calculate the solubility product of AgCl.

Given $E^{\odot}_{Ag \mid Ag \oplus} = -0.799 \text{ V}$

- 8. The standard potential of $\overset{\odot}{OH}$, $Ag_2O(s)|Ag$, and $\overset{\odot}{OH}|O_2$ electrodes are, respectively, 0.344 V and 0.40 V at 25°C; for the formation of Ag_2O , $\Delta H = -29290$ J mol⁻¹ and may be assumed to be independent of temperature. Calculate the temperature at which Ag_2O will begin to decompose in air (20% by volume of O_2).
- 9. When powdered zinc is added to AgNO₃ solution, silver is precipitated according to the reaction 2Ag[⊕] + Zn(s) → Zn²⁺ + 2Ag(s). In an experiment, 100 mL of 1 M solution of AgNO₃ was treated with 5 g of Zn powder. What will be the Ag[⊕] concentration at equilibrium?

Given: $E^{\odot}_{(Ag^{\oplus}|Ag)} = 0.8 \text{ V}, E^{\odot}_{(Zn^{2+}|Zn)} = -0.76 \text{ V}$

- 10. A sample of lead weighing 1.05 g was dissolved in a small quantity of nitric acid to produce and aqueous solution of Pb²⁺ and Ag^{\oplus} (which is present as impurity). The volume of the solution was increased to 350 mL by adding water, a pure silver electrode was immersed in the solution and the potential difference between this electrode and a standard hydrogen electrode was found to be 0.503 V at 25°C. What was the percentage of silver in lead metal? Given: E^{\ominus} of Ag = 0.799 V.
- 11. Calculate the quantity of electricity delivered by a Daniell cell initially containing 1 L, 1 M Cu²⁺ ion and Zn²⁺ ion which is operated until its potential drops to 1.041 V. $(E^{\odot}_{Zn^{2+}+Zn} = -0.76 \text{ V}; E^{\odot}_{Cu^{2+}+Cu} = +0.34 \text{ V})$
- 12. The conductivity of 0.1 M KOH solution is 0.022 S cm⁻¹. When an equal volume of 0.1 M HCl is added, the conductivity decreases to 0.005 S cm⁻¹. A further addition

- of HCl solution, the volume of which is equal to that of the first portion added, the conductivity increases to 0.017 S cm⁻¹. Calculate: (a) Λ_m of KOH (b) Λ_m of KCl
- 13. The resistance of water sample of a swimming pool is determined by using a conductivity cell and was found to be 9200 ohm at 298 K. The same cell dipped in 0.02 M KCl solution has R = 85 ohm. When 500 g of NaCl was dissolved in pool and thoroughly stirred, it showed R = 7600 ohm. If $\Lambda_{\text{m(NaCl)}}$ and $\Lambda_{\text{m(KCl)}}$ are 126.5 and 138.0 S cm² mol⁻¹, respectively, calculate the volume of water in pool.
- 14. The conductivity (κ) of 10^{-3} M Na₂SO₄ solution is 2.6×10^{-4} S cm⁻¹ and increases to 7.0×10^{-4} S cm⁻¹ when the solution is saturated with CaSO₄.

Given: $\lambda_{m(N_a \oplus)}$ and $\lambda_{m(Ca^{2+})}$ are 50 and 120 S cm² m₀|⁻¹, respectively. $\kappa_{H_2O} = 0.50 \times 10^{-6}$ S cm⁻¹

a. κ of only CaSO₄ in the solution

b. Solubility of CaSO₄

c. $K_{\rm sp}$ of CaSO₄.

Calculate

15. $\lambda^{\circ}_{m(Ag^{\oplus})}$ and $\lambda^{\circ}_{m(CrO_4^{2-})}$ are $61.92 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ and $120 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$, respectively. Assuming that Λ_{m} differs very slightly from Λ°_{m} . Calculate the solubility of Ag_2CrO_4 in 10^{-2} M AgNO $_3$ solution.

Given: $\kappa_{(Ag_2CrO_4)} = 4.32 \times 10^{-4} \text{ S m}^{-1}$ and $\kappa_{(Pure\ H_2O)} = 0.86 \times 10^{-4} \text{ S m}^{-1}$ at 300 K

16. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe³⁺. It is found that 5% of Fe³⁺ remains at equilibrium at 25°C. Calculate $E^{\odot}_{(Hg_2^{2+}] Hg}$ assuming that the only reaction that occurs is $2 \text{Hg} + 2 \text{Fe}^{3+} \longrightarrow \text{Hg}_2^{2+} + 2 \text{Fe}^{2+}$

Given: $E^{\odot}_{(\text{Fe}^{3+}|\text{Fe}^{2+})} = 0.77 \text{ V}$

- 17. The overall formation constant for the reaction of 6 mol CN^{Θ} with cobalt (II) is 1×10^{19} . The standard reduction potential for the reaction $[Co(CN)]_6^{3-} + e^- \rightarrow [Co(CN)]_6^{4-}$ is -0.83 V. $E^{\circ}_{Co^{+3}/Co^{+2}} = 1.82$ V. Calculate the overall formation constant of $[Co(CN)]_6^{3-}$.
- 18. A solution containing 1M $XSO_4(aq)$ and 1M $YSO_4(aq)$ is electrolysed. If conc. of X^{2+} is 10^{-z} M when deposition of Y^{2+} and X^{2+} starts simultaneously, calculate the value of Z.

Given:
$$\frac{2.303RT}{F} = 0.06$$

 $E_{X^{2+}|X}^{\circ} = -0.12 \text{ V}; \ E_{Y^{2+}|Y}^{\circ} = -0.24 \text{ V}$

19. Molar conductivity of aqueous solution of HA is $200 \, \text{cm}^2$ mol⁻¹, pH of this solution is 4. Calculate the value of pK_a (HA) at 25°C.

Given: Λ_M^{∞} (NaA) = 100 S cm²mol⁻¹; Λ_M^{∞} (HCl) = 425 S cm² mol⁻¹.

 Λ_M^{∞} (NaCl) = 125 S cm² mol⁻¹

- 20. i. Which of the following oxides is reduced by hydrogen? MgO, CuO and Na2O
 - ii. Which of the following oxides will decompose on heating?

ZnO, CuO, MgO and Ag₂O

iii. The value of E_{ox}° for electrode reactions, Fe \rightarrow Fe²⁺ + 2e⁻, Cu \rightarrow Cu²⁺ + 2e⁻, and Zn \rightarrow Zn³⁺ $+2e^{-}$ are 0.444, -0.337 and 0.763 volts respectively. State which of these metals can replace the other two from the solution of their salts?

ANSWERS

1.
$$3.6 \times 10^{-11} \text{ mol}^2 \text{L}^{-2}$$
 2. 1.08×10^{-14}

4.
$$1.5 \times 10^5 \, \text{L}$$

3.
$$6.57 \text{ S cm}^2 \text{ eq}^{-1}$$
 4. $1.5 \times 10^5 \text{ L}$ 5. $\left[\frac{1000Z}{a+b-c} \right]^2$

6.
$$p^{H} = 4.09$$
 7. $K_{sp} = 1.73 \times 10^{-10}$

$$K_{\rm cm} = 1.73 \times 10^{-10}$$

8.
$$T = 427.03 \text{ K}$$

11.
$$n = 189178.2 \text{ C}$$

12. (a)
$$\Lambda_m(KOH) = 220 \text{ s cm}^2 \text{ mol}^{-1}$$

(b)
$$\Lambda_m(KCl) = 100 \text{ s cm}^2 \text{mol}^{-1}$$

(c)
$$\Lambda_m(HCl) = 403.155 \text{ cm}^2 \text{ mol}^{-1}$$

13.
$$V = 2.01 \times 10^5 \text{ L}$$

14. (a)
$$159.55 \text{ cm}^2 \text{ mol}^{-1}$$
 (b) $S = 1.576 \times 10^{-3} \text{ mol dm}^{-3}$ (c) $K_{\text{sp}} = 4.056 \times 10^{-6} \text{ M}^2$

$$(c) K_{sp} = 4.030 \times 10^{-1} M$$

 $(c) K_{sp} = 4.030 \times 10^{-5} M$

15.
$$S_{(Ag_2CrO_4)} = 1.47 \times 10^{-5} \text{ M}$$
 16. $E^{\circ}_{(Hg_2^{2+}/Hg)} = 0.7976 \text{ V}$

17.
$$K_f = 6 \times 10^{63}$$
 18. $z = 10^{-4}$

18.
$$z = 10^{-4}$$

19.
$$pK_a = 4$$

Solved Examples

Electrochemical Cell

EXAMPLE 3.1

Calculate EMF of the following half cells:

a. Pt,
$$H_2(2 \text{ atm}) \mid HCl(0.02 \text{ M})$$
,

$$E^{\odot} = 0 \text{ V}$$

$$E^{\odot} = 1.36 \text{ V}$$

Sol. a.
$$2H^{\oplus} + 2e^- \longrightarrow H_2$$
 (2 atm)

$$E_{cell} = E_{cell}^{\circ} - \frac{0.059}{2} \log \frac{P_{H_2}}{[H^{\oplus}]^2}$$

$$= 0 - \frac{0.059}{2} \log \frac{2}{(0.02)^2}$$

$$= -\frac{0.059}{2} \log \frac{2}{4 \times 10^{-4}}$$

$$= -\frac{0.059}{2} [\log 10^4 - \log 2]$$

$$= -\frac{0.059}{2} [4 - 0.3]$$

$$= -\frac{0.059}{2} \times 3.7 = -0.0190 \text{ V}$$

$$E_{2\text{H}} \oplus_{|\text{H}_2} = -0.109 \text{ V}$$

b. (Take
$$0.059 \approx 0.06$$
)

$$Cl_2$$
 (10 atm) + $2e^- \longrightarrow 2Cl^{\odot}$ (0.1 M)

$$E_{\text{Cl}_2 \mid 2\text{Cl}} = E_{\text{Cl}_2 \mid 2\text{Cl}} - \frac{0.06}{2} \log \frac{(0.1)^2}{10 \text{ atm}}$$
$$= 1.36 \text{ V} - 0.03 \log 10^{-3}$$
$$= 1.36 + 0.03 \times 3 = 1.45 \text{ V}$$

EXAMPLE 3.2

Calculate pH of the half cell:

$$E^{\odot} = -0.3 \text{V}$$

Sol.
$$E_{2H} \oplus_{H_2} = -0.059 \text{ pH}$$

$$pH = \frac{-0.3}{-0.059} \approx \frac{0.3}{0.06} \approx 5$$

EXAMPLE 3.3

A graph is plotted between E_{cell} and $\log \frac{[Zn^{2+}]}{[Cu^{2+}]}$. The curve is linear with intercept on $E_{\rm cell}$ axis equals to 1.10 V. Calculate $E_{\rm cell}$ for the cell.

$$Zn(s)\parallel Zn^{2+}(0.1\ M)\parallel Cu^{2+}(0.01\ M)\mid Cu$$

Sol. Cell reaction is: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{2} \log \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right]$$
 ...(i)

$$(y = c + mx) \qquad \dots (ii)$$

Equation (i) represents a straight line like Eq. (ii).

$$\therefore$$
 Intercept $(c) = E^{\Theta}_{cell} = 1.10 \text{ V}$

$$\therefore E_{\text{cell}} = 1.10 \text{ V} - \frac{0.059}{2} \log \frac{0.1}{0.01}$$

$$= 1.10 \text{ V} - \frac{0.059}{2} \log 10$$

$$= 1.10 - 0.03$$

$$= 1.07 \text{ V}$$
(Take $0.059 \approx 0.06$)

EXAMPLE 3.4

Given:

$$NO_3^{\odot} \longrightarrow NO_2$$
 (acidic medium),

$$E^{\odot} = 0.8 \text{ V}$$

$$E^{\odot} = 0.74 \text{ V}$$

At what pH the above two half reactions will have same EMF values? Assume the concentration of all the species to be unity. (Take $0.059 \approx 0.06$)

Sol. Balance both equations in acidic medium.

$$NO_3^{\odot} + e^- + 2H^{\oplus} \longrightarrow NO_2 + H_2O$$
 ...(i)

$$NO_3^{\odot} + 6e^- + 7H^{\oplus} \longrightarrow NH_2OH + 2H_2O$$
 ...(ii)

$$\begin{split} E_1 &= E_1^{\odot} - 0.06 \log \frac{[\text{NO}_2]}{[\text{NO}_3^{\odot}][\text{H}^{\oplus}]^2} \quad \begin{bmatrix} [\text{NO}_2] = [\text{NO}_3^{\odot}] \\ &= 1 \text{ M} \end{bmatrix} \\ &= 0.8 - 0.06 \log [\text{H}^{\oplus}]^2 - = 0.8 - 0.06 \times [-\log \text{H}^{\oplus}] \\ &= 0.8 - 0.06 \times 2\text{pH} \\ E_1 &= 0.8 - 0.12 \text{ pH} &(\text{iii}) \\ \text{Similarly, } E_2 \text{ for reaction (ii).} \end{split}$$

$$\begin{split} E_2 &= E^{\odot}_2 - \frac{0.06}{6} \log \frac{[\text{NH}_2\text{OH}]}{[\text{NO}_3^{\odot}][\text{H}^{\oplus}]^7} \quad \begin{bmatrix} [\text{NH}_2\text{OH}] \\ & [\text{NO}_3^{\odot}] = 1 \text{ M} \end{bmatrix} \\ &= 0.74 - 0.01 \log [\text{H}^{\oplus}]^{-7} = 0.74 - 0.01 \times 7 \text{ ($-\log H^{\oplus}$)} \\ &= 0.74 - 0.07 \text{ pH} & \text{(iv)} \end{split}$$

Since $E_1 = E_2$, [equate Eqs. (iii) and (iv)]

$$\therefore 0.8 - 0.12 \text{ pH} = 0.74 - 0.07 \text{ pH}$$
$$\text{pH} = \frac{0.06}{0.05} = 1.2$$

EXAMPLE 3.5

An aqueous solution containing 0.01 M $Fe(ClO_4)_3$, 0.01 M $Fe(ClO_4)_2$, and 0.01 M $HClO_4$ was titrated with a concentrated solution of NaOH at 30°C, so that changes in volumes were negligible. Calculate the redox potential of $Fe^{3+} | Fe^{2+} electrode$ at pH values 2.2, 4.2, 6.0, 8.2, and 10 assuming that new species formed during titration were $Fe(OH)_3$ and $Fe(OH)_2$ only.

Given:

$$E^{\odot}_{\text{Fe}^{3+}|\text{Fe}^{2+}} = 0.77 \text{ V}$$
 $K_{\text{sp}} \text{ of Fe(OH)}_3 = 10^{-37.1}$ $K_{\text{sp}} \text{ of Fe(OH)}_2 = 10^{-18.4}$

Sol

pН	[H [⊕]]	$[\mathbf{OH}] = \frac{K_{\mathbf{w}}}{[\mathbf{H}^{\oplus}]}$	[Fe ³⁺] [OH] ³	[Fe ²⁺] [OH] ²	Result
2.2	10-2.2	10 ^{-11.8}	$10^{-2} \times (10^{-11.8})^3 = 10^{-37.4}$	$10^{-2} \times (10^{-11.8})^2 = 10^{-25.6}$	No precipitation. Ionic product is less
	A Constitution		A CONTRACTOR OF THE SECOND		than $K_{\rm sp}$.
4.2	10-4.2	10-9.8	$10^{-2} \times (10^{-9.8})^3 = 10^{-31.4}$	$10^{-2} \times (10^{-9.8})^2 = 10^{-21.6}$	Fe(OH) ₃ precipitates. Ionic product is greated than K
6	10-6	10 ⁻⁸	$10^{-2} \times (10^{-8})^3 = 10^{-26}$	$10^{-2} \times (10^{-8})^2 = 10^{-18}$	than $K_{\rm sp}$. Both Fe(OH) ₃ and Fe(OH) ₂ precipitate. Ionic product is greater
100		autor i propositio		The state of the s	than $K_{\rm sp}$ of both.

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

$$E^{\odot} = 0.77 \text{ V}$$

When Fe(OH)3 appears,

$$K_{\rm sp} = [{\rm Fe^{3+}}][\stackrel{\odot}{\rm OH}]^3$$

$$\therefore [Fe^{3+}] = \frac{K_{sp}}{[OH]^3} = \frac{[10]^{-37.1}}{[OH]^3}$$

Similarly, when Fe(OH)₂ appears

$$\therefore K_{\rm sp} = [\text{Fe}^{2+}] [\overset{\odot}{\text{OH}}]^2$$

$$\therefore [\text{Fe}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}]^2} = \frac{10^{-18.4}}{[\text{OH}]^2}$$

At pH = 2.2

$$E = 0.77 - \frac{0.06}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$
$$= 0.77 - \frac{0.06}{1} \log \frac{0.01}{0.01} = 0.77 \text{ V}$$

At pH = 4.2

$$E = 0.77 - \frac{0.06}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$= 0.77 - \frac{0.06}{1} \log \frac{0.01}{[10^{-37.1}/(10^{-9.8})^3]}$$

$$= 0.77 - 0.06 \log 10^{5.7}$$

$$= 0.77 - 0.06 \times 5.7 = 0.77 - 0.342 = 0.428$$

At pH = 6

$$E = 0.77 - 0.06 \log \frac{K_{\rm sp} \, \text{Fe}(\text{OH})_2 / [\mathring{\text{OH}}]^2}{K_{\rm sp} \, \text{Fe}(\text{OH})_3 / [\mathring{\text{OH}}]^3}$$

$$= 0.77 - 0.06 \log \frac{10^{-18.4}}{10^{-37.1}} \times [\mathring{\text{OH}}]$$

$$= 0.77 - 0.06 \log 10^{18.7} - 0.06 \log [\mathring{\text{OH}}]$$

$$= 0.77 - 0.06 \times 18.7 - 0.06 \log 10^{-8}$$

$$= 0.77 - 1.122 - 0.06 \times (-8)$$
$$= -0.352 + 0.48$$
$$= 0.128 \text{ V}$$

$$At pH = 8.2$$

$$E = -0.352 - 0.06 \log 10^{-5.8}$$

= -0.352 + 5.8 × 0.06 = -0.352 + 0.348 = -0.004 V

At
$$pH = 10$$

$$E = -0.352 - 0.06 \log 10^{-4}$$

= -0.352 + 0.24 = -0.112 V

EXAMPLE 3.6

The standard potential of a cell using the reaction $2\text{Ni(s)} + \text{O}_2 + 2\text{H}_2\text{O} \Longrightarrow 2\text{Ni(OH)}_2$ is 1.12. The heat of the reaction is $-504.2 \text{ kJ mol}^{-1}$ at 25°C . Calculate the entropy change.

Sol.
$$2\text{Ni}(s) + 4\text{H}_2\text{O} \longrightarrow 2\text{Ni}(\text{OH})_2 + 4\text{H}^{\oplus} + 4e^-$$

 $4\text{H}^{\oplus} + \text{O}_2 + 4e^- \longrightarrow 2\text{H}_2\text{O}$
 $\Delta G^{\odot} = -nFE^{\odot} = -4 \times 96500 \times 1.12 = -432320 \text{ J}$
 $\Delta G^{\odot} = \Delta H^{\odot} - T \Delta S^{\odot}$
 $\Delta S^{\odot} = \Delta H^{\odot} - \Delta G^{\odot}$ $504.2 \times 10^3 \text{ J} - (-43232)$

$$\therefore \Delta S^{\odot} = \frac{\Delta H^{\odot} - \Delta G^{\odot}}{T} = -\frac{504.2 \times 10^{3} \,\text{J} - (-432320)}{298}$$
$$= -241.2 \,\text{J K}^{-1} \,\text{mol}^{-1}$$

EXAMPLE 3.7

The standard potential of a cell using the reaction: $2MnO_4{}^{\circ}(aq)$

$$+3$$
Hg(l) $+$ H₂O \Longrightarrow 2MnO₂(s) $+3$ HgO(s) $+2$ (OH) (aq)

is 0.489 V at 25°C. What is the equilibrium constant of the reaction?

Sol. Anode:
$$MnO_4^{\odot} + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH$$
]× 2

Cathode:
$$Hg(s) + 2OH \longrightarrow H_2O + HgO + 2e^{-}] \times 3$$

$$2\text{MnO}_4^{\odot} + \text{H}_2\text{O} \Longrightarrow 2\text{MnO}_2(\text{s}) + 3\text{HgO} + 2\overset{\odot}{\text{OH}}$$

Cell is in equilibrium,

$$\therefore E_{\rm cell} = 0$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{6} \log K$$

$$\therefore \log K = \frac{nE^{\odot}_{\text{cell}}}{0.059} = \frac{6 \times 0.489}{0.059} = 49.56$$

$$K = 3.631 \times 10^{49}$$

EXAMPLE 3.8

The EMF of the cell:

Ag | AgCl, 0.1 MKCl || 0.1 M AgNO₃ | Ag is 0.45 V. 0.1 M KCl is 85% dissociated and 0.1 M AgNO₃ is 82% dissociated. Calculate the solubility product of AgCl at 25°C.

Sol. It is a concentration cell.

$$\therefore E_{\text{cell}} = 0$$

$$Ag \text{ (Anode)} \longrightarrow Ag^{\oplus} + (c_1) + e^{-}$$

$$Ag^{\oplus}(c_2) + e^{-} \longrightarrow Ag \text{ (Anode)}$$

$$Ag^{\oplus}(c_2) \longrightarrow Ag^{\oplus}(c_1)$$

 $0.1 \text{ M AgNO}_3 = 0.1 \text{ M Ag}^{\oplus}$

Since it is 82% ionized

$$\therefore$$
 Ag ^{\oplus} (cathode) = 0.1 × 0.82

$$c_2 = 0.082 \text{ M}$$

$$\therefore E_{\text{cell}} = 0 - \frac{0.0591}{1} \log \frac{[Ag^{\oplus}(c_1)]}{[Ag^{\oplus}(c_2)]}$$

$$0.45 = -\frac{0.0591}{1} \log \frac{[Ag^{\oplus}(c_1)]}{0.082}$$

$$\frac{0.45 \times 1}{0.0591} = \log \frac{0.082}{[Ag^{\oplus}(c_1)]} = 7.627$$

Antilog
$$(7.627 \times 10^7) = 3.99 \times 10^7$$

$$\therefore [Ag^{\oplus}(c_1)] = \frac{0.082}{3.99 \times 10^7} = 2.055 \times 10^{-9} M$$

Since it is 85% dissociated

$$C[C1^{\circ}] = 0.1 \times 0.85 = 0.085 \text{ M}$$

:.
$$K_{\rm sp}({\rm AgCl}) = [{\rm Ag}^{\oplus}] [{\rm Cl}^{\odot}]$$

= $(1.9 \times 10^{-9}) (0.085)$

$$K_{\rm sp} = 1.615 \times 10^{-10}$$

EXAMPLE 3.9

Calculate the potential corresponding to the following cell. Given

Pt | Co²⁺(2.0 M), Co³⁺ (0.01 M) || Cr³⁺ (0.5 M), Cr₂O₇²⁻ (4.0 M), H^{\oplus} (1.5 M) | Pt $E_{Co^{2+}|Co^{3+}}^{\ominus} = -1.82 \text{ V}$

$$E^{\odot}_{\text{Cr}_2\text{O}_7^{2-}|\text{Cr}^{3+}} = +1.33 \text{ V}$$

Sol.
$$Co^{2+} \longrightarrow Co^{3+} + e^{-}] \times 6$$

$$14H^{\oplus} + Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6\text{Co}^{+2} + 14\text{H}^{\oplus} + \text{Cr}_2\text{O}_7^{2-} \longrightarrow 6\text{Co}^{+3} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

$$E^{\odot}_{\text{cell}} = -1.82 + 1.33 \text{ V} = -0.49$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.0591}{6} \log \frac{[\text{Co}^{3+}]^6 [\text{Cr}^{3+}]^2}{[\text{Co}^{2+}]^6 [\text{Cr}_2 \text{O}_7^{2-}] [\text{H}^{\oplus}]^{14}}$$

=
$$-0.49 - \frac{0.0591}{6} \log \frac{[10^{-2}]^6 [0.50]^2}{[2.0]^6 [4.0][1.5]^{14}} = -0.32 \text{ V}$$

EXAMPLE 3.10

Knowing that $K_{\rm sp}$ for AgCl is 1.0×10^{-10} , calculate E for a silver/silver chloride electrode immersed in 1.00 M KCl at 25° C. $E_{\rm Ap\Phi \mid Ag}^{\odot} = 0.799$ V.

Sol.
$$K_{\rm sp}({\rm AgCl}) = [{\rm Ag}^{\oplus}] [{\rm Cl}^{\ominus}], \ {\rm KCl} = 1.00 \ {\rm M}$$

$$\therefore$$
 [Cl ^{\odot}] = 1.00 M

$$\therefore [Ag^{\oplus}] = \frac{K_{\rm sp}}{[C1^{\odot}]} = \frac{1.0 \times 10^{-10}}{1.00} = 1.0 = 10^{-10}$$

$$Ag^{\oplus} + e^{-} \longrightarrow Ag$$

$$E^{\odot}_{Ag^{\oplus}+Ag} = 0.799 \text{ V}$$

$$\therefore E = E^{\odot} - \frac{0.059}{1} \log \frac{1}{[Ag^{\oplus}]}$$

$$= 0.799 - \frac{0.059}{1} \log \frac{1}{(0.10 \times 10^{-10})}$$

$$= 0.799 - 0.592 = 0.207 \text{ V}$$

EXAMPLE 3.11

Consider the following half reactions:

PbO₂(s) + 4H[⊕](aq) + SO₄²⁻(aq) + 2e⁻ →
PbSO₄(s) + 2H₂O
$$E^{\odot} = +1.70 \text{ V}$$
PbSO₄(s) + 2e⁻ → Pb(s) + SO₄²⁻(aq) $E^{\odot} = -0.31 \text{ V}$

- **a.** Calculate the value of E^{\odot} for the cell.
- **b.** Calculate the voltage generated by the cell if $[H^{\oplus}] = 0.10 \text{ M}$ and $[SO_4^{2-}] = 2.0 \text{ M}.$
- c. What voltage is generated by the cell when it is at chemical equilibrium?

Sol.

a.
$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{Cathode}} - E^{\ominus}_{\text{Anode}}$$

 $= 1.70 - (-0.31) = 2.01 \text{ V}$
 $PbO_2 + 4H^{\oplus} + SO_4^{2-} + 2e^{-} \longrightarrow PbSO_4 + 2H_2O$
 $Pb + SO_4^{2-} \longrightarrow PbSO_4$
 $PbO_2 + Pb + 4H^{\oplus} + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$

b.
$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{1}{[H^{\oplus}]^4 [SO_4^{2-}]^2}$$

= $2.01 - \frac{0.059}{2} \log \frac{1}{(0.14)^4 (2.0)^2}$

c. When cell is at equilibrium, $E_{\text{cell}} = 0$

EXAMPLE 3.12

The EMF of the cell

 $Ag \mid 0.1 \text{ (N) } AgNO_3 \parallel 1 \text{ (N) } KBr, AgBr(s) \mid Ag \text{ was found to be}$ –0.64 V at 298 K. 0.1 N AgNO $_{\! 3}$ is 81.3% dissociated and 1 N KBr is 75.5% dissociated.

Calculate:

- a. Solubility
- b. Solubility product of AgBr at 298 K

Sol. Ag | 0.1 N AgNO₃ || 1 N KBr, AgBr (s) | Ag The above cell is concentration cell

$$\therefore E^{\odot}_{\text{cell}} = 0$$

$$\begin{array}{c}
Ag^{\oplus}_{(\text{anode})} \longrightarrow Ag^{\oplus}(0.1 \text{ N}) + e^{-} \\
Ag^{\oplus}_{(\text{cathode})} + e^{-} \longrightarrow Ag_{(\text{cathode})} \\
Ag^{\oplus}_{(\text{cathode})} \longrightarrow Ag^{\oplus}(0.1 \text{ N})
\end{array}$$

Since AgNO₃ is 81.3% ionized

$$\therefore [Ag^{\oplus}]_a = 0.1 \times 0.813 = 0.0813 \text{ N}$$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{1} \log \left[\frac{Ag_{\text{(anode)}}^{\oplus}}{Ag_{\text{(cathode)}}^{\oplus}} \right]$$

$$-0.64 = 0 - 0.059 \log \frac{0.0813}{[Ag_{(cathode)}^{\oplus}]}$$

$$\therefore [Ag^{\oplus}]_{\text{(cathode)}} = 3.2 \times 10^{-12} \text{ M}$$

Since 1 N KBr is 75.5 % dissociated

$$\therefore [Br^{\odot}] = 1 \times 0.755 = 0.755 M$$

$$K_{\rm sp} = [Ag^{\oplus}] [Br^{\odot}] = 3.2 \times 10^{-12} \times 0.755$$

= 2.416 × 10⁻¹²

$$S = \sqrt{2.416 \times 10^{-12}}$$
$$= 1.554 \times 10^{-6} \text{ M}$$

EXAMPLE 3.13

For the cell Zn | ZnCl₂(m) | AgCl, E is 1.24V at 25°C and 1.260V at 35°C of $m = 10^{-3}$. Write down the cell reaction and calculate ΔG , ΔH , and ΔS at 25°C.

Sol. Cell reaction

$$Zn \longrightarrow Zn^{2+} | + 2e^{-}$$

 $2AgCl + 2e^{-} \Longrightarrow 2Ag + 2Cl^{\odot}$
 $Zn(s) + 2AgCl(s) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2Cl^{\odot}(aq)$

$$\frac{\Delta E}{\Delta T} = \frac{1.26 - 1.24}{308 - 298} = 2 \times 10^{-3} \text{ V degree}^{-1}$$

$$\Delta G^{\odot} \text{ (at 298 K)} = -nFE^{\odot} = -2 \times 96500 \times 1.24$$

$$= -239320 \text{ J}$$

$$= -239.32 \text{ kJ}$$

$$\Delta S^{\odot} = nF \left(\frac{\partial E}{\partial T} \right) = 2 \times 96500 \times 2 \times 10^{-3} = 386 \text{ J}$$

$$\Delta G = \Delta H - T \Delta S$$

$$-239320 = \Delta H - 298 \times 386$$

$$\therefore \Delta H = -124292 \text{ J}$$

EXAMPLE 3.14

A saturated calomel electrode is coupled through a salt bridge with a grant in with a quinhydrone electrode dipping in 0.1 M NH₄Cl. The observed ENTE observed EMF at 25°C is 0.152 V. Find the dissociation constant of NH₄OH. The oxidation potential of saturated caloniel electrode = -0.699 V at 25°C.

Sol. For the cell: Saturated calomel $\parallel 0.1 \text{ MNH}_4\text{Cl} \mid \text{H}_2\text{Q}, \text{Q} \mid^{\text{pt}}$

$$E_{\text{cell}} = E_{\text{quinhydrone electrode}} - E_{\text{saturated calomel}}$$

$$E_{\text{cell}} = 0.152$$

$$\begin{bmatrix} E_{\text{saturated calomel (oxid)}} = -0.242 \text{ V} \\ E_{\text{saturated calomel (red)}} = 0.242 \text{ V} \end{bmatrix}$$

$$(E_{\text{saturated calomel (red)}} = 0.242 \text{ V}$$

$$(E_{\text{quinhydrone}} = 0.6994 - 0.059 \text{ pH})$$

$$E^{\odot}_{\text{avid}} = -0.6994$$
, so $E^{\odot}_{\text{Red}} = 0.6994$

$$\therefore E_{\text{cell}} = E_{\text{quinhydrone}} - E_{\text{saturated calomel}}$$

$$0.152 = 0.6994 - 0.059$$
pH $- 0.242$

$$\therefore pH = \frac{0.457 - 0.152}{0.059} = 5.17$$

For 0.1 M NH₄Cl, salt of $\rm S_A/W_B$ which on hydrolysis gives NH₄OH

$$pH = \frac{1}{2} (pK_w - pK_b - \log c)$$

$$5.17 = \frac{1}{2} (14 - pK_b - \log 0.1)$$

Solving, we get $K_b = 2.18 \times 10^{-5}$

EXAMPLE 3.15

Two weak acid solutions HA_1 and HA_2 with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm and 25°C) and are interconnected through a salt bridge. Find the EMF of the cell.

For hydrogen electrode at 1 atm and 25°C

$$E_{\rm red} = -0.059 \text{ pH}$$

Assuming the degree of dissociation to be small, pH of a weak acid,

$$pH = \left(\frac{1}{2}pK_a - \frac{1}{2}\log c\right)$$

.. For electrode at acid HA1,

$$E_{\text{redc}} = -0.059 \text{ pH} = -0.0599 \left(\frac{1}{2} \text{ p} K_{a_1} - \frac{1}{2} \log c \right)$$
$$E_{\text{redc}} = -\frac{0.059}{2} (p K_{a_1} - \log c)$$
$$= -\frac{0.059}{2} (3 - \log c)$$

Similarly, for hydrogen electrode at acid HA2,

$$E_{\text{toda}} = -\frac{0.059}{2} (5 - \log c)$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{Anode}}$$

$$= -\left[\frac{0.059}{2}(3 - \log c)\right] - \left[\frac{0.059}{2}(5 - \log c)\right]$$

$$= -0.0295 \times 3 + 0.0295 \times 5$$

$$= 0.0295 \times (5-3) = 0.0295 \times 2 = 0.059 \text{ V}$$

EXAMPLE 3.16

Find the solubility of AgCl in 0.1 M CaCl₂. $E^{\odot}_{Ag^{\oplus} \mid Ag} = 0.799 \text{ V}$ and that of AgCl | Ag = 0.222 V.

$$Ag \longrightarrow Ag^{\oplus} + e^{-}$$

$$AgCl + e^{-} \longrightarrow Ag + Cl^{\ominus}$$

$$AgCl \longrightarrow Ag^{\oplus} + Cl^{\ominus}$$

$$E^{\ominus} = 0.222 - 0.799 = -0.577$$

$$(:: E_{cell} = 0)$$

$$E^{\odot} = 0.059 \log K_{\rm sp} (n=1)$$

$$-0.577 = 0.059 \log K_{\rm sp}$$

$$\therefore K_{\rm sp} = 1.66 \times 10^{-10}$$

Let S M is the solubility of AgCl in 0.1 M CaCl₂

$$AgCI \longrightarrow Ag^{\oplus} + CI^{\ominus}$$

$$S$$
 S S S

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^{\Theta}$$
0.1 0 0

Total
$$C1^{\odot} = (S + 0.2) \text{ M}$$

$$K_{\rm sp} = [Ag^{\oplus}][C1^{\ominus}] = S(S + 0.2)$$

$$\therefore 1.66 \times 10^{-10} = (S^2 + 0.2S) [S^2 < 1]$$

$$\therefore S = \frac{1.66 \times 10^{-10}}{2} = 8.3 \times 10^{-10} \text{ M}$$

EXAMPLE 3.17

The EMF of the cell:

Ag | $Ag_2CrO_4(s)$, K_2CrO_4 (0.01 M) || $AgNO_3(0.01 \text{ M})$ | Ag is 206.5 mV. Calculate the solubility of Ag_2CrO_4 in 1 M Na_2CrO_4 solution.

Sol. It is a concentration cell, therefore, $E^{\ominus}_{cell} = 0$.

$$\begin{array}{c} Ag_{(Anode)} \longrightarrow Ag_{(Anode)}^{\oplus} + e^{-} \\ Ag_{(Cathode)}^{\oplus} + e^{-} \longrightarrow Ag_{(Cathode)} \\ \hline Ag_{(Cathode)}^{\oplus} \longrightarrow Ag_{(Anode)}^{\oplus} \end{array}$$

$$E = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log \left[\frac{Ag^{\oplus}_{\text{(Anode)}} \text{ (let it is } x)}{Ag^{\oplus}_{\text{(cathode)}} \text{ (which is 0.01 M)}} \right]$$

$$0.2065 = -\frac{0.059}{1} \log \frac{x}{0.01 \,\mathrm{M}}$$

$$-\frac{0.2065}{0.059} = -\log x - \log 10^{-2}$$

$$\log x = -2 - 3.5 = -5.5 = \overline{6}.5$$

Taking Antilog $\Rightarrow x = 3.163 \times 10^{-6} \text{ M}$

$$Na_2CrO_4 \rightleftharpoons 2Na^{\oplus} + CrO_4^{2-}$$

Total
$$[CrO_4^{2-}] = [1 + 0.01] = 1 M$$

$$Ag_2CrO_4 \Longrightarrow 2Ag^{\oplus} + CrO_4^2$$

$$K_{\rm sp} = (x)^2 (0.01) = (3.163 \times 10^{-6})(0.01) = 10^{-13}$$

$$K_{sp} = [Ag^{\oplus}][CrO_4^{2-}]$$

$$K_{\rm sp} = S^2 \times (1 \text{ M})$$

$$[Ag^{\oplus}] = S = \sqrt{K_{sp}}$$

[Ag
$$\oplus$$
] in 1 M Na₂CrO₄ = $\sqrt{K_{\rm sp}}$

$$= \sqrt{10^{-13}}$$

$$= \sqrt{10 \times 10^{-14}}$$

$$= 3.16 \times 10^{-7} \text{ M}$$

EXAMPLE 3.18

The EMF of a galvanic cell

Pt | H₂(1 atm) | HCl(1 M) | Cl₂(g) | Pt is 1.29 V.

Calculate the partial pressure of Cl₂(g).

$$E^{\odot}_{\text{Cl}_2|\text{Cl}^{\odot}} = 1.36 \text{ V}$$

Sol. Cell reaction:

$$\frac{1}{2} H_2(g) \longrightarrow 2H^{\oplus} + e^{-} \qquad E^{\ominus}_{\text{oxid}} = 0 \text{ V}$$

$$2Cl_2(g) + e^{-} \longrightarrow Cl^{\ominus} \text{ (aq)} \qquad E^{\ominus}_{\text{red}} = 1.36 \text{ V}$$

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow H^{\oplus} \text{ (aq)} + Cl^{\ominus} \text{ (aq)}$$

$$E^{\ominus}_{\text{cell}} = 1.36 \text{ V}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{1} \log \frac{[\text{H}^{\oplus}][\text{Cl}^{\odot}]}{[p_{\text{H}_2}]^{1/2} [p_{\text{Cl}_2}]^{1/2}}$$

$$1.29 = 1.36 - \frac{0.059}{1} \log \left(\frac{1 \times 1}{1 \times [p_{\text{Cl}_2}]^{1/2}}\right)$$

Solve,
$$p_{\text{Cl}_2} = 4.24 \times 10^{-3} \text{ atm}$$

EXAMPLE 3.19

Calculate the potential of silver electrode in a saturated solution of AgBr ($K_{\rm sp}=6\times10^{-13}$) containing 0.1 M KBr. $E^{\odot}_{\rm Ag\oplus~|Ag}=0.80~\rm V$.

Sol. AgBr
$$\Longrightarrow$$
 Ag $^{\oplus}$ + Br $^{\odot}$
 $K_{\rm sp} = [{\rm Ag}^{\oplus}] [{\rm Br}^{\odot}]$
 $[{\rm Ag}^{\oplus}] = \frac{K_{\rm sp}}{[{\rm Br}^{\odot}]} = \frac{6 \times 10^{-13}}{0.1} = 6 \times 10^{-12} \,\mathrm{M}$
 ${\rm Ag}^{\oplus} + e^{-} \longrightarrow {\rm Ag}$
 $E = E^{\odot} - \frac{0.059}{1} \log \frac{1}{[{\rm Ag}^{\oplus}]} = 0.80 - 0.059 \log \frac{1}{[6 \times 10^{-12}]}$
 $= 0.80 - 0.059 [\log 10^{12} - \log 6]$
 $= 0.80 - 0.059 [12 - 0.7782]$
 $= 0.80 - 0.059 \times 11.2218$
 $= 0.80 - 0.6662 = 0.138$

EXAMPLE 3.20

A solution of Fe²⁺ is titrated potentiometrically using Ce⁴⁺ solution. Calculate the EMF of the redox electrode thus formed when

- a. 50% of Fe²⁺ is titrated
- **b.** 90% of Fe²⁺ is titrated
- c. 110% titration is done

Given: $E_{\text{Fe}^{2+}|\text{Fe}^{3+}}^{\ominus} = -0.77 \text{ V}$ and

$$Fe^{2+} Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}, K = 10^{14}$$

Sol.

a. During titration, the redox electrode is Pt $\mid Fe^{2+}$, Fe^{3+} electrode

$$E = E^{(\cdot)}_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$$

At 50% titration, $[Fe^{3+}] = [Fe^{2+}]$

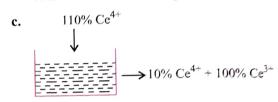
$$\therefore E = E^{\odot} = -0.77 \text{ V}$$

b. At 90% titration, $\frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{90}{10}$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$$

Initial 90 10 Final 510 90

$$E = -0.77 - 0.059 \log 9 = -0.826 \text{ V}$$



At 110% titration, the electrode becomes,

Pt | Ce³⁺, Ce⁴⁺ electrode, where
$$\frac{[Ce^{4+}]}{[Ce^{3+}]} = \frac{10}{100}$$

Cell reaction:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-} \qquad E^{\ominus}_{\text{oxid}} = -0.77 \text{ V}$$

$$Ce^{4+} + e^{-} \longrightarrow Ce^{3+} \qquad E^{\ominus}_{\text{Red}} = 1$$

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+} E_{cell}^{\odot} = (x - 0.77) V$$

At equilibrium, $E_{cell} = 0$

$$E = E_{\text{cell}}^{\ominus} - \frac{0.059}{1} \log K$$

$$E_{\text{cell}}^{\ominus} = \frac{0.059}{1} \log 10^{14} = 0.826$$

$$\therefore x - 0.77 = 0.822 \Rightarrow x = 1.596$$

$$E^{\odot}_{Ce^{4+}/Ce^{3+}} = 1.596 \text{ V}$$

$$\therefore E^{\odot}_{\text{Ce}^{3+}/\text{Ce}^{4+}} = -1.596 \text{ V}$$

So at 110% titration.

$$E_{\text{Ce}^{3+}/\text{Ce}^{4+}} = E^{\odot}_{\text{Ce}^{3+}/\text{Ce}^{4+}} - 0.059 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$
$$= -1.596 - 0.059 \log \left(\frac{10}{100}\right)$$
$$= -1.596 + 0.059 = -1.537 \text{ V}$$

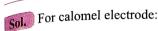
EXAMPLE 3.21

Find the EMF of the cell at 25°C.

Decinormal Buffer Quinhydrone calomel electrode pH = 3.5 electrode

 E_{red}^{\odot} (quinhydrone electrode) = 0.699 V

 E_{red}^{\odot} (calomel electrode) = +0.268 V



$$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg + 2Cl^{\odot}$$

For decinormal calomel electrode: [Cl[⊙]] = 0.1 N

$$E_{\text{(red)}} \text{ Calomel} = E^{\odot} - \frac{0.059}{2} \log [\text{Cl}^{\odot}]^2$$

= $0.268 - \frac{0.059}{2} \log [0.1]^2$
= $0.268 + 0.059 = 0.327 \text{ V}$

For quinhydrone electrode, i.e., Pt | H₂Q | H[⊕] | Q

$$2H^{\oplus} + Q + 2e^{-} \rightleftharpoons H_2Q$$

$$E_{\text{red(quinhydrone)}} = E^{\odot} - \frac{0.059}{2} \log \frac{1}{[H^{\oplus}]^2}$$

$$= 0.699 - 0.059 \text{ pH}$$

$$= 0.699 - 0.059 \times 3.5$$

$$E_{\text{cell}} = 0.4929 - 0.327 = 0.1659$$

EXAMPLE 3.22

The EMF of the following cell is found to be - 0.46 V:

$$\begin{array}{c|c} \text{Pt, H}_2 & \text{NaHSO}_4 & \text{Na}_2 \text{SO}_4 & Z n^{+2} \\ \hline & (0.4 \text{ M}) & (6.44 \times 10^{-3} \text{ M}) & (0.3 \text{ M}) \end{array} \bigg| Z n$$

If the standard electrode potential of Zinc is -0.763 V, find the value of K_2 for H_2SO_4 , where

$$K_2 = \frac{[H^{\oplus}][SO_4^{2-}]}{[HSO_4^{\odot}]}$$

Sol. At anode:
$$H_2 \rightleftharpoons 2H^{\oplus} + 2e^{-}$$

At cathode:
$$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$$
 $E = -0.46 \text{ volt}$

[negative value shows cell is not feasible]

Cell reaction:
$$H_2 + Zn^{2+} \rightleftharpoons Zn + 2H^{\oplus}$$

$$E = E^{\odot} - \frac{0.059}{2} \log \frac{[H^{\oplus}]^2}{[Zn^{2+}]}$$

$$-0.46 = -0.763 - \frac{0.059}{2} \log \frac{[H^{\oplus}]^2}{0.3}$$

Solve,
$$[H^{\oplus}] = 4 \times 10^{-6}$$

$$HSO_4^{\ominus} \longrightarrow H^{\oplus} + SO_4^{2-}$$

$$K_2 = \frac{[\text{H}^{\oplus}][\text{SO}_4^{\ 2}]}{[\text{HSO}_4^{\ \Theta}]} = \frac{(4 \times 10^{-6}) (6.44 \times 10^{-3})}{(0.4)} = 6.44 \times 10^{-8}$$

EXAMPLE 3.23

The EMF of the following cell is observed to be 0.118 V at 25°C:

 $^{\mbox{\sc lf}\,30}\mbox{\sc mL}$ of 0.2 M NaOH is added to the negative terminal of the battery, find the EMF of the cell.

Sol. It is concentration cell, therefore, $E^{\odot} = 0$.

$$E_{\text{cell}} = -\frac{0.059}{1} \log \frac{[\text{H}^{\oplus}]_{\text{a}}}{[\text{H}^{\oplus}]_{\text{c}}}$$

$$0.118 = -0.059 \log \frac{[H^{\oplus}]_a}{0.1}$$

$$\therefore [H^{\oplus}]_{a} = 10^{-3} M$$

$$HA \longrightarrow H^{\oplus} + A^{\ominus}$$

$$A \longrightarrow A$$

At equilibrium
$$(0.1 - 10^{-3})$$
 10^{-3} 10^{-3}

$$K_{\rm a} = \frac{[{\rm H}^{\oplus}][{\rm A}^{\odot}]}{[{\rm HA}]} = \frac{(10^{-3})^2}{0.1} = 10^{-5}$$

When NaOH is added to HA, acidic buffer is formed at negative electrode.

$$HA + NaOH \longrightarrow NaA + H_2O$$

Initial
$$0.01$$

Final $(0.01 - 0.006)$

= 0.004
Buffer equation:
$$pH = pK_a + log \frac{[Salt]}{[Acid]}$$

$$H^{\oplus} = K_a \times \frac{[Acid]}{[Salt]} = 10^{-5} \times \frac{0.004}{0.006} = 6.67 \times 10^{-6}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\odot} - \frac{0.059}{1} \log \frac{(6.67 \times 10^{-6})}{0.1} = 0.246 \text{ V}$$

EXAMPLE 3.24

Find the standard electrode potential of I, | 21° if the equilibrium constant for the reaction $I_2 + I^{\odot} \longrightarrow I_3^{\odot}$ is 703. The standard electrode potential of I₃ | 3I^o is 0.5355 V. Also give the electrode reaction.

Sol. Anode: (a) $3I^{\odot} \longrightarrow I_{2}^{\odot} + 2e^{-}$

Cathode (c)
$$I_2 + 2e^- \longrightarrow 2I^{\odot}$$

$$I_2 + I^{\odot} \longrightarrow I_3^{\odot}$$

At equilibrium
$$E_{\text{cell}} = 0$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{2} \log K_{\text{eq}}$$

$$\therefore E^{\odot}_{\text{cell}} = \frac{0.059}{2} \log K_{\text{eq}}$$

$$E_{l_2|2l^{\Theta}}^{\Theta} - E_{l_3^{\Theta}/3l^{\Theta}}^{\Theta} = \frac{0.059}{2} \log 703$$

$$E_{1,|2|}^{\odot} = 0.5355 = \frac{0.059}{2} \log 703$$

$$E^{\odot}_{l_2 \mid 2l^{\odot}} = \frac{0.059}{2} \log 703 + 0.5355$$

$$=\frac{0.059}{2} \times 2.846 + 0.5355 = 0.619 \text{ V}$$

EXAMPLE 3.25

A silver electrode dipping in $AgNO_3$ solution (0.1 M) is combined through salt bridge with a hydrogen electrode dipping in a solution of pH = 3 (at 25°C). If the standard reduction potential of the silver electrode is 0.799 V, what is the EMF of the cell?

Sol.
$$Ag |AgNO_3(0.1M)| |H^{\oplus}| pH = 3| H_2$$

 $E_{Ag^{\oplus}|Ag}^{\odot} = 0.99 \text{ V}; E_{cell}^{\odot} = ?$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{H}_2} - E^{\circ}_{\text{Ag}}$$
$$= 0 - 0.799 \text{ V} = -0.779 \text{ V}$$

Since the reduction potential of Ag^{\oplus} > Reduction potential of H_2

If polarity reversed, $E^{\odot} = 0.799 \text{ V}$

So cell would be

$$H_2 | (H^{\oplus}) (pH = 3) || AgNO_3 (0.1 M) | Ag$$

Cell reaction:

$$\frac{1}{2} \operatorname{H}_2 \longrightarrow \operatorname{H}^{\oplus} + e^{-}$$

$$\frac{Ag^{\oplus} + e^{-} \longrightarrow Ag}{\frac{1}{2}H_{2} + Ag^{\oplus} \longrightarrow H^{\oplus} + Ag}$$

$$E_{\text{cell}} = E^{\odot}_{\text{cell}} - \frac{0.059}{1} \log \frac{[\text{H}^{\oplus}]}{[\text{Ag}^{\oplus}]}$$
$$= 0.799 - \frac{0.059}{1} \log \frac{10^{-3}}{0.1}$$
$$= 0.799 - 0.059 \log 10^{-2}$$

 $= 0.799 + 0.059 \times 2 = 0.917 \text{ V}$

EXAMPLE 3.26

The EMF of a galvanic cell composed of two hydrogen electrodes is 177 mV. If the solution at one of the electrodes has $[H^{\oplus}] = 10^{-3}$, find the $[H^{\oplus}]$ at the other electrode.

Sol.
$$H_2 \mid H_1^{\oplus} (10^{-3}) \mid H_2^{\oplus} (x) \mid H_2$$

$$E = -0.059 \text{ (pH}_1 - \text{pH}_2) = -0.059 \text{ (3} - \text{pH}_2)$$

$$177 \times 10^{-3} \text{ V} = -0.177 + \text{pH}_2 \times 0.059$$

$$0.059 \text{ pH}_2 = 0.177 + 0.177$$

$$pH_2 = \frac{0.354}{0.059} = 6$$

$$[H^{\oplus}] = 10^{-6} \text{ M}$$

EXAMPLE 3.27

The EMF of the cell:

Pt | Ce⁴⁺(90%), Ce³⁺(10%) | Normal calomel electrode is 1.464 V at 25°C. Find the value of equilibrium constant of the reaction:

$$2Ce^{3+} + 2H^{\oplus} \longrightarrow 2Ce^{4+} + H_2$$

The electrode potential of the normal calomel electrode is +0.28 V.

Sol.
$$E_{\text{cell}} = E_{\text{c}} - E_{\text{a}} = 1.464 \text{ V}$$

$$E_{\text{Ce}^{4+}|\text{Ce}^{3+}} = E_{\text{Ce}^{4+}|\text{Ce}^{3+}}^{\circ} - \frac{0.059}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Cr}^{4+}]}$$
$$= E_{\text{Ce}^{4+}|\text{Ce}^{3+}}^{\circ} - \frac{0.059}{1} \log \frac{10}{90}$$

$$E_{\text{cell}} = E_{\text{cal}} - E_{\text{Ce}^{4+} | \text{Ce}^{3+}}$$

$$1.464 = E_{\text{cal}} - \left[\left(E^{\odot}_{\text{ Ce}^{4+}|\text{ Ce}^{3+}} - 0.059 \log \frac{1}{8} \right) \right]$$

$$1.464 = 0.28 - \left(E^{\odot}_{\text{Ce}^{4+}|\text{Ce}^{3+}} - 0.059 \log \frac{1}{8} \right)$$

$$E^{\odot}_{Ce^{4+}|Ce^{3+}} = -1.24 \text{ V}$$

Now,
$$2Ce^{3+} + 2H^{\oplus} \rightleftharpoons 2Ce^{4+} + H_2$$

At Eq,
$$E_{\text{cell}} = 0$$
.

$$\therefore E^{\odot} = \frac{0.059}{2} \log K$$

$$2Ce^{3+} \longrightarrow 2Ce^{4+} + 2e^{-}$$
 (Oxidation)

At cathode:
$$2H^{\oplus} + 2e^{-} \longrightarrow H_{2}$$

(Reduction)

Cell reaction:
$$2Ce^{3+} + 2H^{\oplus} \longrightarrow 2Ce^{4+} + H$$
,

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{red (cathode)}} - E^{\odot}_{\text{red (anode)}}$$
$$= E^{\odot}_{\text{red (H}_2)} - E^{\odot}_{\text{red (Ce}^{4+} \mid \text{Ce}^{3+})}$$
$$= 0 - (-1.24) = 1.24$$

$$\therefore E^{\odot} = \frac{0.059}{2} \log K$$

$$1.24 = \frac{0.059}{2} \log K$$

$$\log K = 42.03 \Rightarrow K = 1.08 \times 10^{42}$$

EXAMPLE 3.28

A hydrogen electrode placed in a buffer solution of sodium cyanide and HCN in the ratio of x:y and y:x has electrode potential value a and b volts, respectively, at 25°C. If the difference a-b=35.52 mV, what is the ratio of y:x.

Sol. Acidic buffer (NaCN + HCN)

$$pH = pK_a + \log\left[\frac{Salt}{Acid}\right]$$

Pt
$$|H_2|$$
 Buffer (NaCN+HCN) Buffer NaCN+HCN $pH_1 = pK_a + \log \frac{x}{y}$ $pH_2 = pK_a + \log \frac{y}{x}$ $pH_3 = 0.059 \text{ pH}_3$ $pH_4 = 0.059 \text{ pH}_4$ $pH_5 = 0.059 \text{ pH}_5$ $pH_6 = 0.059 \text{ pH}_6$ $pH_6 = 0.059 \text{ pH}_6$ $pH_6 = 0.059 \text{ pH}_6$ $pK_6 = 0.059 \text{ pH}_6$

EXAMPLE 3.29

Two electrochemical cells are assembled in which the following reactions occur:

$$V^{2+} + VO^{2+} + 2H^{\oplus} \longrightarrow 2V^{3+} + H_2O$$

$$V^{3+} + Ag^{\oplus} + H_2O \longrightarrow VO^{2+} + 2H^{\oplus} + Ag(s)$$

Calculate E^{\odot} for half reaction $V^{3+} + e^{-} \longrightarrow V^{2+}$

Given:
$$E^{\ominus}_{(Ag^{\oplus}|Ag)} = 0.799 \text{ V}$$

 $E^{\ominus} = E^{\ominus}_{V^{4+}|V^{3+}} - E^{\ominus}_{V^{3+}|V^{2+}} = 0.616 \text{ V}$
 $E^{\ominus} = E^{\ominus}_{Ag^{\oplus}|Ag} - E^{\ominus}_{V^{4+}|V^{3+}} = 0.439 \text{ V}$

Sol.
$$V^{3+} + e^- \longrightarrow V^{2+}$$

$$E^{\Theta} =$$

Cell Reaction:
$$V^{2+} + VO^{2+} + 2H^{\oplus} \longrightarrow 2V^{3+} + H_2O$$

Half cell reaction:

$$V^{2+} \longrightarrow V^{3+} + e^{-}$$

$$\frac{V^{4+} \text{ from } (VO^{2+}) + e^{-} \longrightarrow V^{3+}}{V^{2+} + V^{4+} \longrightarrow V^{3+}}$$

$$E^{\odot}_{\text{cell}} = E^{\odot}_{V^{4+} | V^{3+}} - E^{\odot}_{V^{3+} | V^{2+}}$$

= 0.616 (given) ...(i)

Second cell

$$V^{3+} \longrightarrow V^{4+} + e^{-}$$

$$Ag^{\oplus} + e^{-} \longrightarrow Ag$$

$$V^{3+} + Ag^{\oplus} \longrightarrow V^{4+} + Ag$$

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{Ag} \oplus /\text{Ag}} - E^{\odot}_{\text{V}^{4+} | \text{V}^{3+}}$$

$$0.439 = 0.791 = E^{\odot}_{V^{4+}|V^{3+}}$$

$$E_{V^{4+}|V^{3+}}^{\odot} = 0.36 \text{ V}$$

Substituting in Eq. (i)

$$E^{\odot}_{\text{cell}} = E^{\odot}_{V^{4+}|V^{3+}} - E^{\odot}_{V^{3+}|V^{2+}}$$

$$0.616 = 0.36 - E^{\odot}_{V^{3+}|V^{2+}}$$

$$E^{\Theta}_{V^{3+}|V^{2+}} = -0.256$$

EXAMPLE 3.30

Predict whether or not Cl_2 would disproportionate in cold alkaline medium. The standard reduction potentials of $\text{Cl}_2 \mid \text{Cl}^\odot$ and $\text{ClO}^\odot \mid \text{Cl}_2$ are 1.36 V and 0.40 V, respectively.

Sol. Anode:
$$4 \overset{\bigcirc}{O} H + Cl_2 \longrightarrow 2ClO^{\ominus} + 2H_2O + 2e^-$$
Cathode: $Cl_2 + 2e^- \longrightarrow 2Cl^{\ominus}$

$$E^{\ominus} = E^{\ominus}_{c} - E^{\ominus}_{a}$$

$$= 1.36 - 0.4 = 0.96$$

 E^{\odot} = positive, cell is feasible.

Disproportionate of Cl₂ (i.e., simultaneous oxidation and reduction of Cl₂) is feasible.

EXAMPLE 3.31

What would be the electrode potential of a silver electrode dipped in a saturated solution of AgCl in contact with 0.1 M KCl solution at 25°C?

$$E^{\odot}_{Ag^{\bigoplus}/Ag} = 0.799 \text{ V}$$
 $K_{sp} \text{ of } AgCl = 1 \times 10^{-10}$

Sol, Ag | AgCl, 0.1 M KCl

$$E = E^{\odot} - \frac{0.059}{1} \log \frac{1}{[Ag^{\oplus}]}$$

$$[Cl^{\odot}] = 0.1$$

$$[Ag^{\oplus}] = \frac{K_{\rm sp}}{[Cl^{\odot}]} = \frac{10^{-10}}{0.1} = 10^{-9}$$

$$E = 0.799 - \frac{0.059}{1} \log \frac{1}{[10^{-9}]}$$

$$= 0.799 - 0.059 \times 9 = 0.799 - 0.531 = 0.268 \text{ V}$$

EXAMPLE 3.32

 E^{\odot} of some elements are given as:

$$I_{2} + 2e^{-} \longrightarrow 2I^{\odot}$$

$$MnO_{4}^{\odot} + 8H^{\oplus} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O, \quad E^{\odot} = 1.52 \text{ V}$$

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$$

$$Sn^{4+} + 2e^{-} \longrightarrow Sn^{2+}$$

$$E^{\odot} = 0.1 \text{ V}$$

- a. Select the strongest reductant and weakest oxidant among these elements.
- **b.** Select the weakest reductant and strongest oxidant among these elements.

Sol.

a. Higher the positive value for oxidation potential, more is the tendency for oxidation and the element will act as a stronger reductant.

or

Lower the value for reduction potential, more is the tendency for oxidation and the element will act as a stronger reductant. Maximum E^{\odot}_{oxid} (-0.1 V) or minimum E^{\odot}_{red} (0.1 V) for Sn²⁺ to Sn⁴⁺.

Strongest reductant: Sn2+

Weakest oxidant: Sn4+

b. E_{red}° value (1.52 V) is highest for MnO₄ $^{\circ}$ to Mn²⁺. More the tendency to undergo reduction and more the element will act as a stronger oxidant.

∴ Strongest oxidant: MnO₄[©]

Weakest reductant: Mn²⁺

Note: Stronger the oxidant, weaker the conjugate reductant and vice versa.

EXAMPLE 3.33

Select the spontaneous reactions from the changes given below

a.
$$Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$$

b.
$$2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^{\odot}$$

c.
$$\operatorname{Sn}^{4+} + 2\operatorname{I}^{\odot} \longrightarrow \operatorname{Sn}^{2+} + \operatorname{I}_{2}$$

d.
$$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^{\odot}$$

Sol. For (a) Sn⁴⁺ reduces to Sn²⁺ and Fe²⁺ oxidizes to Fe³⁺.

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{red}} + E^{\odot}_{\text{oxid}}$$

$$= E^{\odot}_{\text{Sn}^{4+} | \text{Sn}^{2+}} + E^{\odot}_{\text{Fe}^{2+} | \text{Fe}^{3+}}$$

$$= 0.1 \text{ V} - 0.77 \text{ V} = -0.67 \text{ V}$$

Hence, E_{cell}^{\odot} is negative and the cell is non-spontaneous.

For (b), I_2 reduces to $2I^{\odot}$ and Fe^{2+} oxidizes to Fe^{3+} .

$$E^{\odot}_{cell} = E^{\odot}_{red} + E^{\odot}_{oxid}$$

$$= E^{\odot}_{I_2 \mid 2I^{\odot}} + E^{\odot}_{Fe^{2+} \mid Fe^{3+}}$$

$$= 0.54 \text{ V} - 0.77 \text{ V} = -0.23 \text{ V}$$

Hence, $E_{\text{cell}}^{\ominus}$ is negative and the cell is non-spontaneous.

For (c), Sn^{4+} reduces to Sn^{2+} and $2I^{\odot}$ oxides to I_{γ} .

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{red}} + E^{\odot}_{\text{oxid}}$$

$$= E^{\odot}_{\text{Sn}^{4+} | \text{Sn}^{2+}} + E^{\odot}_{2I^{\odot} | I_{2}}$$

$$= 0.1 \text{ V} - 0.54 \text{ V} = -0.44 \text{ V}$$

Hence, $E^{\odot}_{\rm cell}$ is negative and the cell is non-spontaneous.

For (d), I_2 reduces to $2I^{\odot}$ and Sn^{2+} oxides to Sn^{4+} .

$$\therefore E^{\odot}_{\text{cell}} = E^{\odot}_{\text{red}} + E^{\odot}_{\text{oxid}} = E^{\odot}_{\text{I}_{2} | 2I^{\odot}} + E^{\odot}_{\text{Sn}^{2+} | \text{Sn}^{4+}}$$
$$= 0.54 \text{ V} - 0.1 \text{ V} = 0.44 \text{ V}$$

Hence, E^{\odot}_{cell} is positive and the cell is spontaneous.

EXAMPLE 3.34

Two metals M_1 and M_2 have $E_{red}^{\odot} = -0.76$ V and 0.80 V, respectively. Which will liberate $H_2(g)$ from H_2SO_4 ?

Given:

$$M_1^{n+} + ne^- \longrightarrow M_1$$

$$E_{red}^{\circ} = -0.76 \text{ V}$$

$$M_2^{n+} + ne^- \longrightarrow M_2$$

$$2H^{\oplus} + 2e^- \longrightarrow H_2(g)$$

$$E_{red}^{\circ} = 0.80 \text{ V}$$

$$E_{red}^{\circ} = 0.0 \text{ V}$$

Sol.

a. Now constructing a cell of metal M_1 with H_2SO_4 , $2M_1 + nH_2SO_4 \longrightarrow (M_1)_2(SO_4)_n + nH_2$...(i) $[M_1 \text{ undergoes oxidation to } M_1^{2+} \text{ and } 2H^{\oplus} \text{ undergoes}]$ reduction to H_2]

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{red}} + E^{\odot}_{\text{oxid}}$$

$$= E^{\odot}_{2H^{\oplus}|H_{2}} + E^{\odot}_{M_{1}|M_{1}^{2+}}$$

$$= 0 + 0.76 = 0.76 \text{ V}$$

Since E^{\odot}_{cell} is positive and reaction (i) is spontaneous therefore, M_1 will liberate H_2 from H_2SO_4 .

b. Now constructing a cell of metal M_2 with H_2SO_4 . $2M_2 + nH_2SO_4 \longrightarrow (M_2)_2(SO_4)_n + nH_2$...(ii) $[M_2$ undergoes oxidation to M_2^{2+} and $2H^{\oplus}$ undergoes reduction to H_2]

$$\therefore E^{\odot}_{\text{cell}} = E^{\odot}_{\text{red}} + E^{\odot}_{\text{oxid}}$$

$$= E^{\odot}_{2\text{H}} \oplus_{|\text{H}_{2}} + E^{\odot}_{\text{M}_{2} | \text{M}_{2}}^{2+}$$

$$= 0 - 0.80 \text{ V}$$

Since E^{\odot}_{cell} is negative and reaction (ii) is non-spontaneous, thus, M_2 will not liberate H_2 , from H_2 , G_0

EXAMPLE 3.35

Determine whether $O_2(g)$ can oxidize sulphate $(SO_4^{\ 2-})$ ion to peroxodisulphate $(S_2O_8^{\ 2-})$ ion or not in an acidic solution with $O_2(g)$ being reduced to water.

Given:
$$E^{\odot}_{O_2|2H_2O} = 1.20 \text{ V}$$
 and $E^{\odot}_{S_2O_8^{2-}|2SO_4^{2-}} = 2.0 \text{ V}$

Sol. The oxidation reaction of SO_4^{2-} to $S_2O_8^{2-}$ and reduction reaction of O_2 to H_2O are as below:

(Reduction)
$$O_2(g) + 4H^{\oplus}(aq) + 4e^- \longrightarrow 2H_2O$$
,

(Oxidation)
$$4SO_4^{2-} \longrightarrow 2S_2O_8^{2-} + 4e^- \quad E^{\odot}_{\text{oxid}} = -2.0 \text{ V}$$

Net reaction:
$$O_2(g) + 4SO_4^{2-} + 4H^{\oplus} \longrightarrow 2S_2O_8^{2-} + 2H_2O_8^{2-}$$

$$E^{\odot}_{\text{cell}} = E^{\odot}_{\text{red}} + E^{\odot}_{\text{oxid}}$$

$$= E^{\odot}_{\text{O}_2 \mid 2\text{H}_2\text{O}} + E^{\odot}_{\text{SO}_4^{2-} \mid \text{S}_2\text{O}_8^{2-}}$$

$$= 1.20 \text{ V} - 2.0 \text{ V} = -0.8 \text{ V}$$

Since E^{\odot}_{cell} is negative, thus, O_2 will not oxidize SO_4^{2-10} $S_2O_8^{2-1}$.

EXAMPLE 3.36

Quinones are good electron acceptors, partly because reduction restores aromaticity.

$$\begin{array}{c}
O \\
O \\
O \\
P-Quinone
\end{array}$$

$$\begin{array}{c}
OH \\
OH \\
Hydroquinon
\end{array}$$

$$Q + 2e^- + 2H^{\oplus} \longrightarrow H_2Q$$

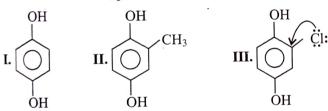
give the decreasing order of $E^{\odot}_{\text{reduction}}$ of the following

Sol.

a. Decreasing order or $E^{\odot}_{\text{reduction}}$

 $\Pi > I > \Pi$

- **b.** ||| > || > |
- **c.** | | > |
- a. After reduction, products are:



Reactivity order: II > I > IIIStability order: III > I > II

III is more stable due to +R (or +M) effect of Cl than +I and H.C. effect of CH_3 .

More stable the product means faster the reduction of quinone to hydroquinone and therefore higher $E^{\odot}_{\rm red}$ value

- :. Decreasing order of E^{\odot}_{red} value in (a): III > I > II.
- b. Stability order: I > II > IIIReactivity order: III > II > I(III) is more easily reduced to

two aromatic rings which have more resonance energy and greater stability than the reaction of (I) and (II), which would generate only one benzene ring.

Both (I) and (II) on reduction give one benzene ring, but (II) is less stable (more reactive) than I because adjacent (C=O) groups in (II) make it less stable.

The reaction is represented as follows:

 $Q + 2H^{\oplus} + 2e^{-} \rightarrow H_{2}O$

 \therefore Reduction potential $(E^{\odot}_{O \mid H_2O})$: III > II > I.

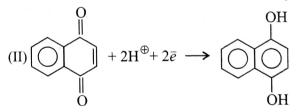
c. Stability order: I > II Reactivity order: II > I Standard reduction potential $(E^{\ominus}_{O+H_2O})$: II > I

(I)
$$OH$$

$$+ 2H^{\oplus} + 2e^{-} \longrightarrow OH$$

$$(I_{1})$$

$$9,10-Dihydroxyanthracene$$



(I) has two individual benzene rings whose combined resonance energy along with that of two (C=O) groups is more than the resonance energy of three benzene rings of reduced product (I_1) .

Electrolysis and Electrolytic Cells

EXAMPLE 3.37

Express each of the following combinations of electrical units as a single unit:

- a. Volt-ampere
- b. Ampere-second
- c. Volt ampere⁻¹
- d. Joule volt-1
- e. Watt (ampere-ohm)-1
- f. Joule second-1
- g. Joule (ampere-second)⁻¹
- **h.** Joule (ampere⁻² second⁻¹)

Sol.

- a. Watt
- **b.** Coulomb
 - c. Ohm
- d. Coulomb

- e. Ampere
- f. Watt
- g. Volt
- h. Ohm

EXAMPLE 3.38

A resistance heater was wound around a 5.0 g metallic cylinder. A current of 0.84 A was passed through the heater for 20 s while the drop in voltage across the heater was 5.0 V. The temperature change of the cylinder was from 25°C before the heating period and 35°C at the end. If the heat loss is neglected, what is the specific heat of the cylinder metal in cal g⁻¹ K⁻¹.

Sol. Energy input =
$$I \cdot V \cdot t$$

= (0.84 A) (5 V) (20 s)
= $\frac{84 \text{ J}}{4.18 \text{ L cal}^{-1}} \approx 20 \text{ calorie}$

Also

Energy input = Mass × Specific heat × Temperature rise
=
$$(5.0 \text{ g})$$
 (Specific heat) × $[(35-25) \text{ K}]$
= $50 \times \text{specific heat}$

$$20 \text{ cal} = 50 \times \text{specific heat}$$

Specific heat =
$$\frac{20}{50}$$
 = 0.4 cal g⁻¹ K⁻¹

EXAMPLE 3.39

In a zinc manganese dioxide dry cell, the anode is made up of Zn and cathode of carbon rod surrounded by a mixture of MnO₂, carbon, NH₄Cl, and ZnCl₂ in aqueous base. The cathodic reaction is:

$$ZnMnO_2(s) + Zn^{2+} + 2e^- \longrightarrow ZnMn_2O_4(s)$$

 8.7 g of MnO_2 is taken in the cathodic compartment. How many days will the dry cell continue to give a current of $9.65 \times 10^{-3} \text{ A}$? (Atomic weight of Mn = 55) (Mw of MnO₂ = 87 g mol⁻¹)

Sol. When MnO₂ will be used up in cathodic process, the dry cell will stop to produce current.

(n factor for
$$MnO_2 = 3 - 2 = 1$$
)

$$\therefore$$
 1 Eq of MnO₂ = 1 mol of MnO₂ = 87 g

$$(1 \text{ F} = 96500 \text{ C} = 1 \text{ mol of MnO}_2 = 87 \text{ g})$$

$$8.7 \text{ g of MnO}_2 = 9650 \text{ C} = I \times t$$

$$= 9.65 \times 10^{-3} \,\mathrm{A} \times t \,\mathrm{(s)}$$

$$\therefore t = \frac{9650 \text{ C}}{9.65 \times 10^{-3} \text{ A}} = 10^6 \text{ s} = \frac{10^6}{60 \times 60 \times 24}$$
$$= 11.57 \text{ days}$$

Alternatively, use the direct formula

$$W_{\text{MnO}_2} = \frac{Ew \times I \times t}{96500 \text{ C}}$$

EXAMPLE 3.40

An aqueous solution of NaCl on electrolysis gives $H_2(g)$, $Cl_2(g)$, and NaOH according to the reaction:

$$2Cl^{\odot} + 2H_2O \longrightarrow 2OH + H_2(g) + Cl_2(g)$$

A direct current of 96.5 A with current efficiency of 50% is passed through 100 L solution of NaCl (20% by weight).

- a. Write down the reactions taking place at the electrodes
- b. How long will it take to produce 35.5 g of Cl₂?
- c. What will be the molarity of the solution with respect to OH ion?
- d. What will be the final pH of the solution?
 Assume no loss in volume due to evaporation.

Sol.

- a. At cathode: $2Cl^{\odot} \longrightarrow Cl_2 + 2e^-$ At anode: $2H_2O + 2e^- \longrightarrow 2OH + H_2$
- **b.** $[2e^- = 2 \text{ F} = 2 \times 96500 \text{ C} \equiv 1 \text{ mol of Cl}_2 = 71 \text{ g}]$ or $1 \text{ F} = 96500 \text{ C} = 1 \text{ Eq of Cl}_2 = 35.5 \text{ g}$ Since current efficiency is 50%

$$\therefore$$
 Current = $96.5 \times \frac{50}{100} = \frac{96.5}{2}$

Use direct relation,

$$W_{\text{Cl}_2} = \frac{Ew_{(\text{Cl}_2)} \times I \times t}{96500 \,\text{C}}$$

$$35.5 \text{ g} = \frac{35.5 \text{ g} \times 96.5/2 \times t}{96500 \text{ C}}$$

$$\therefore t = \frac{96500 \times 35.5 \times 2}{35.5 \times 96.5} = 2000 \text{ s}$$

$$2000 \text{ s} = \frac{2000}{3600} = 0.55 \text{ h}$$

c. Eq of $\stackrel{\odot}{OH}$ formed = Eq of Cl_2 = $\frac{35.5 \text{ g}}{35.5 \text{ g}}$ = 1 Eq

$$[\overset{\circ}{O}H] = \frac{\text{Equivalent}}{V_{\text{I}}} = \frac{1}{100 \,\text{L}} = 10^{-2} \,\text{N}$$

d.
$$pOH = -\log [10^{-2}] = 2 \Rightarrow pH = 14 - 2 = 12$$

EXAMPLE 3.41

A constant current was flown for 1 min through a solution of KI. At the end of experiment, liberated I_2 consumed 150 mL of 0.01 M solution of $Na_2S_2O_3$ following the reaction:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^{\odot} + S_4O_6^{2-}$$

What was the average rate of current flow in ampere?

Sol.
$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^ \left(n \text{ factor } = \frac{2}{2} = 1\right)$$

 $mEq of KI = mEq of I_2 liberated$

$$= mEq of Na2SO3$$

=
$$150 \text{ mL} \times 0.01 \times 1(n \text{ factor})$$

$$= 1.5 \text{ mEg}$$

$$[1 F = 96500 C = 1 Eq of S_2O_3^{2-}]$$

$$1.5 \times 10^{-3} \text{ Eq} = 96500 \text{ C} \times 1.5 \times 10^{-3} \text{ Eq}$$

$$\Rightarrow I \times t$$
 (s) = $I \times 60$

$$I = \frac{96500 \text{ C} \times 1.5 \times 10^{-3} \text{ Eq}}{60 \text{ s}} = \frac{965}{400} = 2.4125 \text{ A}$$

EXAMPLE 3.42

Aqueous solution of *m*-dinitroso benzene was electrolyzed for 2 hours passing current of 2 A with efficiency of 90%. Calculate the amount of 3-aminoaniline.

$$(Mw = 108 \text{ g mol}^{-1})$$

$$=\frac{2\times2\times3600\times0.90}{96500}=0.134$$

Mol of product obtained =
$$\frac{\text{Equivalent}}{n \text{ factor}} = \frac{0.134}{8}$$

Weight of product = Mol ×
$$M_W$$

= $\frac{0.134}{9}$ × 108 = 1.812 g

EXAMPLE 3.43

A 35% solution of LiCl was electrolyzed by using a 2.5 A current for 0.8 h. Assuming the current efficiency of 90%, find the mass of LiOH produced at the end of electrolysis. (Atomic mass of Li = 7)

Sol. Number of Faradays =
$$\frac{90}{100} \left(\frac{2.5 \times 0.8 \times 3600}{96500} \right)$$

$$= 0.067 F$$

$$Ew = Mw$$
 of LiOH = $7 + 16 + 1 = 24$ g mol⁻¹

(n factor = 1)

$$W_{\text{LiOH}} = E_W \times \text{Eq}$$

= 24 × 0.067 = 1.61 g

EXAMPLE 3.44

A current of $10 \, \text{A}$ is employed to plate nickel in NiSO₄ bath. The current efficiency with respect to Ni plating is 60%.

- a. How many grams of Ni is plated on the cathode per hour?
- b. What is the thickness of the plating if the cathode consists of a sheet of metal 4.0 cm² which is coated on both faces?
- c. What is the volume of H₂ (STP) evolved during above electrolysis?

Sol. At cathode:
$$Ni^{2+} + 2e^{-} \longrightarrow Ni$$

 $2H^{\oplus} + 2e^{-} \longrightarrow H_{2}$

Both reactions (reduction) occur simultaneously in the given case.

Number of Faradays

$$= \frac{It}{96500} = \frac{10 \times 60 \times 60}{96500}$$
 F = 0.373 F

2 F = 1 mol Ni

$$0.373 \text{ F} = \frac{0.373}{2} \times 59 \text{ g} = 11.00 \text{ g}$$

a. For 60% efficiency, weight of Ni plated

$$=\frac{60}{100} \times 11 = 6.6 \text{ g Ni}$$

b. Mass = Area \times Thickness \times Density

$$6.6 = 4 \times (2t) \times 1.25$$

(Here t = thickness)

$$\Rightarrow t = \frac{6.6}{10} = 0.66 \text{ cm} = 6.6 \text{ mm}$$

c. $2 F = 1 \text{ mol} = 22400 \text{ mL H}_2$

$$0.373 \text{ F} \equiv \frac{22400 \times 0.373}{2} = 4177.6 \text{ mL} \equiv 4.178 \text{ L}$$

EXAMPLE 3.45

A certain amount of charge is passed through acidulated water. A total of 504 mL of hydrogen and oxygen were collected at STP. Find the magnitude of charge that is passed during electrolysis in coulombs.

Sol.
$$1 \text{ F} = 1 \text{ Eq of O}_2 + 1 \text{ Eq of H}_2$$

$$= 5.6 L O_2 + 11.2 L of H_2 = 16.8 L$$

$$16.8 \times 10^3 \text{ mL} \Rightarrow 1 \text{ F}$$

$$504 \text{ mL} \Rightarrow \frac{1 \times 504}{16.8 \times 10^3}$$

$$= 0.03 \text{ F} = 0.03 \times 96500 = 2895 \text{ C}$$

Note:

Electro-synthesis: It is a method of producing chemical compounds through non-spontaneous reactions carried out by electrolysis. The above example is an illustration of electrosynthesis. Similarly, by electrolyzing a solution of $MnSO_4$ in H_2SO_4 , MnO_2 may be produced at anode.

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2(s) + 4H^{\oplus} + 2e^{-}$$

$$\Rightarrow$$
 2 F = 1 mol of MnSO₄ = 1 mol of MnO₂

EXAMPLE 3.46

During the electrolysis of water, a total volume of 33.6 mL of hydrogen and oxygen gas was collected at STP. Find the amount of electricity that passed during electrolysis.

Sol. Cathode:
$$2H^{\oplus} + 2e^{-} \longrightarrow H_2$$

$$\Rightarrow$$
 2 F = 1 mol of H₂ = 22400 mL

or 1 F = 0.5 mol of
$$H_2 = 11200 \text{ mL}$$

Anode:
$$4\overset{\odot}{O}H \longrightarrow O_2 + 4e^- + 2H_2O$$

$$\Rightarrow$$
 4 F = 1 mol of O₂ = 22400 mL

or 1 F = 0.25 mol of
$$O_2 = 11200 \text{ mL}$$

From two electrode reactions, it is clear that hydrogen and oxygen are evolved in the mole ratio of 2:1, hence their volumes will also be in the same ratio.

$$\Rightarrow$$
 Volume of H₂ = 2/3(33.6) = 22.4 mL

As $2 F = 22400 \text{ mLH}_2$

 \Rightarrow 0.002 F of charge is passed through the electrolytic cell.

 \Rightarrow Amount of electricity = 0.002 × 96500 C = 193.0 C

EXAMPLE 3.47

During an electrolysis of conc H_2SO_4 , perdisulphuric acid $(H_2S_2O_8)$ and O_2 are formed in equimolar amount. The moles of H_2 that will be formed simultaneously will be

a. Thrice that of O,

b. Twice that of O₂

c. Equal to that of O₂

d. Half of that of O2

Sol.

a. This is a special case of electrolysis where two products are being obtained at anode.

At anode:

$$4\overset{\circ}{\mathrm{OH}} \longrightarrow \mathrm{O_2} + 2\mathrm{H_2O} + 4e^- \qquad ...(i)$$

$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^- \qquad ...(ii)$$

1 mol O_2 requires 4 F electricity and 1 mol $S_2O_8^{2-}$ ($\equiv H_2S_2O_8$) requires 2 F electricity.

So, if x mol of O_2 are being produced, electricity being passed at anode is:

 $4x \text{ (for O}_2) + 2x \text{ (3 for S}_2\text{O}_8^{2-}) = 6x \text{ F}$

At cathode:

$$2H^{\oplus} + 2e^{-} \longrightarrow H_2$$
 ...(iii)

2 F electricity $\equiv 1 \mod H_2$ is produced

 \Rightarrow 6x F electricity $\equiv 1 \mod H_2$ is produced

 \Rightarrow Moles of H₂ produced at cathode = 3 mol of O₂ produced at anode.

EXAMPLE 3.48

A current of 1.0 A is passed for 96.5 s through a 200 mL solution of 0.05 M LiCl solution. Find

a. The volume of gases produced at STP

b. The pH of solution at the end of electrolysis

Sol. Number of faradays passed

$$= \frac{It}{96500} = \frac{1.0 \times 96.5}{96500} = 10^{-3} \text{ F}$$

Cathode: $2H^{\oplus} + 2e^{-} \longrightarrow H_2$

(Li[®] will remain in solution)

 $2 F \equiv 1 \text{ mol of H}_2$

or
$$1 \times 10^{-3} \text{ F} \equiv 0.5 \times 10^{-3} \text{ mole of H}_2$$

 $\equiv 0.5 \times 10^{-3} \times 22400 \text{ mL H}_2 \text{ at STP}$
 $\equiv 11.2 \text{ mL H}_2 \text{ STP}$

Anode: $2C1^{\odot} \longrightarrow C1_2 + 2e^{-}$

(O₂ will be not be liberated due to over potential)

$$\Rightarrow$$
 2 F = 1 mol of Cl₂

or
$$1 \times 10^{-3} \text{ F} \equiv 0.5 \times 10^{-3} \text{ mol of Cl}_2$$

 $\equiv 0.5 \times 10^{-3} \times 22400 \text{ mL Cl}_2 \text{ at STP}$
 $= 11.2 \text{ mL Cl}_2 \text{ at STP}$

In solution, Li[⊕] and OH are left.

To calculate the pH of solution, first calculate the millimoles of H^\oplus ions electrolyzed.

 \Rightarrow mmoles of H^{\oplus} ions electrolyzed = mEq of H^{\oplus} ions electrolyzed = Number of faradays passed = 10^{-3} F

Since H_2O produces equal number of H^\oplus and $\stackrel{\odot}{OH}$ ions. mmoles $\stackrel{\odot}{OH}$ ions left in excess = 10^{-3}

$$\Rightarrow [\text{OH}] \approx \frac{10^{-3}}{200/1000} = 5 \times 10^{-3} \,\text{M}$$

[Neglect OH from dissociation of H₂O]

$$\Rightarrow$$
 pOH = $-\log (5 \times 10^3) = 3 - \log 5 = 2.3$

$$\Rightarrow$$
 pH = 14 - pOH = 14 - 2.3 = 11.7

Exercises

Single Correct Answer Type

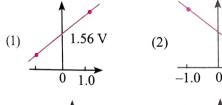
Electrochemical Cell

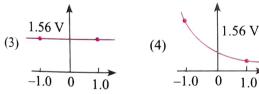
- 1. Which of the following statement is correct?
 - (1) Cathode is -ve terminal in both, galvanic and electrolytic
 - (2) Anode is +ve terminal in both, galvanic and electrolytic
 - (3) Cathode and anode are -ve terminal in electrolytic and galvanic cell
 - (4) Cathode and anoce are +ve terminal in electrolytic and galvanic cell.
- 2. Which of the following statements is correct about Galvanic cell?
 - (1) It converts chemical energy into electrical energy.
 - (2) It converts electrical energy into chemical energy.
 - (3) It converts metal from its free state to the combined state.
 - (4) It converts electrolyte into individual ions.
- 3. Which graph correctly correlates $E_{\rm cell}$ as a function of concentrations for the cell

$$Zn(s) + 2Ag^{\oplus}(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s),$$

 $E^{\circ}_{cell} = 1.56 \text{ V}$

$$Y$$
-axis: E_{cell} , X -axis: $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{\oplus}]^2}$





4. Given the listed standard electrode potentials, what is E° for the cell:

$$\begin{split} 4 \text{BiO}^{\oplus} \left(\text{aq} \right) + 3 \text{N}_2 \text{H}_5^{\oplus} (\text{aq}) & \longrightarrow 4 \text{Bi(s)} + 3 \text{N}_2 (\text{g}) \\ & + 4 \text{H}_2 \text{O(l)} + 7 \text{H}^{\oplus} (\text{aq}) \\ \text{N}_2 (\text{g}) + 5 \text{H}^{\oplus} (\text{aq}) + 4 e^- & \longrightarrow \text{N}_2 \text{H}_5^{\oplus} (\text{aq}), E^{\circ} = -0.23 \text{ V} \\ \text{BiO}^{\oplus} (\text{aq}) + 2 \text{H}^{\oplus} (\text{aq}) \ 3 e^- & \longrightarrow \text{Bi(s)} + \text{H}_2 \text{O(l)}, \end{split}$$

$$E^{\circ} = +0.32 \text{ V}$$

$$(1) + 0.55$$

(2) +0.34

$$(3) + 1.88$$

(4) + 0.09

5. What is the standard electrode potential for the reduction of HClO?

HClO(aq) + H[⊕](aq) 2
$$e^-$$
 → Cl^Θ(aq) + H₂O(l)
Given Cr²⁺(aq) → Cr³⁺(aq) e^- , $E^\circ = 0.41$ V
HClO(aq) + H[⊕](aq) + 2Cr²⁺(aq) → 2Cr³⁺(aq) + Cl^Θ(aq)
+ H₂O(l), $E^\circ = 1.80$

(2) 1.54

$$(3)$$
 1.22

(4) 0.90

6. The E° for the following cell is +0.34 V.

$$In(s) \mid In(OH)_3(aq) \parallel SbO_2^{\Theta}(aq) \mid Sb(s).$$

Using $E^{\circ} = -1.0 \text{ V}$ for the In (OH)₃ | In couple.

Calculate E° for the SbO₂ $^{\ominus}$ | Sb half-reaction:

$$(1)$$
 -1.34

(2) + 0.66

$$(3) + 0.82$$

(4) -0.66

7. From the following half-cell reactions and their standard potentials, what is the smallest possible standard e.m.f. for spontaneous reactions?

$$PO_4^{3-}(aq) + 2H_2O(1) + 2e^- \longrightarrow HPO_3^{2-} + 3OH(aq);$$

$$PbO_2(s) + H_2O(l) + 2e^- \longrightarrow PbO(s) + 2OH(aq);$$

$$IO_3^{\Theta}(aq) + 2H_2O(l) + 4e^- \longrightarrow IO^{\Theta}(aq) + 4OH(aq);$$

$$(1) +0.00$$

(2) +0.74

$$(3) +0.56$$

(4) +0.28

8. Determine which substance is the best reducing agent in Q. 7.

(1)
$$HPO_3^{2-}$$

(2) PO₄³⁻ (4) IO₃[⊖]

9. Consider the following half-cell reactions and associated standerd half-cell potentials and determine the maximum voltage that can be obtained by combination resulting in spontaneous processes:

$$\mathrm{AuBr_4^{\ominus}(aq)} + 3e^- \longrightarrow \mathrm{Au(s)} + 4\mathrm{Br^{\ominus}(aq)}; E^\circ = -0.86 \ \mathrm{V}$$

$$Eu^{3+}(aq) + e^{-} \longrightarrow Eu^{2+}(aq); \quad E^{\circ} = -0.43 \text{ V}$$

$$Sn^{2+}(aq) + 2e^{-} \longrightarrow Sn(aq); E^{\circ} = -0.14 \text{ V}$$

$$IO^{\Theta}(aq) + H_2O(1) + 2e^- \longrightarrow I^{\Theta}(aq) + 2OH(aq);$$

$$E^{\circ} = +0.49 \text{ V}$$

$$(1) + 0.72$$

(2) + 1.54

$$(3) + 1.00$$

(4) + 1.35

10. A solution containing H^\oplus and D^\oplus ions is in equilibrium with a mixture of H₂ and D₂ gases at 25°C. If the partial pressures of both gases are 1.0 atm, find the ratio of $[D^{\oplus}]/[H^{\oplus}]$:

(Given:
$$E_{D^{\oplus}/D_2}^{\circ} = -0.003 \text{ V}$$
)

- (1) 1.23
- (2) 1.12
- (3) 0.11
- (4) 1.0
- 11. The E° at 25°C for the following reaction is 0.55. Calculate ΔG° in kJ/mol:

$$4\text{BiO}^{\oplus}(\text{aq}) + 3\text{N}_2\text{H}_5^{\oplus} \longrightarrow 4\text{Bi}(\text{s}) + 3\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$$
+ 7H[⊕]

- (1) -637
- (2) -424
- (3) -106
- (4) -318.5
- 12. A large quantity of cobalt metal was dropped into a solution containing Ag[⊕], Fe³⁺ and Cu²⁺, all at unit concentration. If $E^{\circ} (Ag^{\oplus}/Ag) = 0.799 \text{ V},$

 $E^{\circ}(\text{Fe}^{3+}, \text{Fe}^{2+}/\text{Pt}) = 0.77 \text{ V},$

 $E^{\circ}(Cu^{2+}/Cu) = 0.34 \text{ V},$

 $E^{\circ}(\text{Fe}^{3+}/\text{Fe}) = -0.04 \text{ V},$

 $E^{\circ}(Cu^{2+}/Cu^{\oplus}/Pt) = 0.153 \text{ V} \text{ and}$

 $E^{\circ}(\text{Co}^{2+}/\text{Co}) = 0.28 \text{ V}$, then the solution would contian

(1) Ag, Fe and Cu

(2) Ag, Fe and Cu[⊕]

(3) Fe²⁺, Cu and Co²⁺

(4) Fe $^{2+}$, Cu, Ag and Co $^{2+}$

13. Given: $E^{\circ}(\operatorname{Sn}^{2+}, \operatorname{Sn}^{4+}/\operatorname{Pt}) = 0.15 \text{ V},$

 $E^{\circ}(Hg_2^{2+}, Hg^{2+}/Pt) = 0.92 \text{ V}$ and

 $E^{\circ}(Pb^{2+}, H^{+}/PbO_{2}) = 1.45 \text{ V}$. Based on this data, which of the following statements is correct?

- (1) Sn⁴⁺ is a stronger oxidizing agent than Pb⁴⁺
- (2) Sn^{2+} is a stronger reducing agent than Hg_2^{2+}
- (3) Hg²⁺ is a stronger oxidizing agent than Pb⁴⁺
- (4) Pb²⁺ is a stronger reducing agent than Sn²⁺
- 14. Indicator electrode is:
 - (1) SHE
- (2) Calomel electrode
- (3) Ag/AgCl electrode (4) Quinhydrone electrode
- **15.** Given that:

$$I_2 + 2e^- \longrightarrow 2I^{\odot};$$
 $E^{\odot} = 0.54 \text{ V}$

 $Br_2 + 2e^- \longrightarrow 2Br^{\odot};$

 $E^{\odot} = 1.69 \text{ V}$

Predict which of the following is true.

- (1) I^{\odot} ions will be able to reduce bromine.
- (2) Br[⊙] ions will be able to reduce iodine.
- (3) Iodine will be able to reduce bromine.
- (4) Bromine will be able to reduce iodide ions.
- 16. An electrochemical cell stops working after some time because
 - (1) Electrode potential of both the electrodes becomes zero.
 - (2) Electrode potential of both the electrodes becomes equal.
 - (3) One of the electrode is eaten away.
 - (4) The reaction starts proceeding in opposite direction.
- 17. Which of the following statements is correct for a galvanic cell?
 - (1) Reduction occurs at cathode
 - (2) Oxidation occurs at anode
 - (3) Electrons flow from anode to cathode
 - (4) All the statements are correct
- **18.** Given $E^{\odot}_{Ag^{\oplus}|Ag} = +0.80 \text{ V}$; $E^{\odot}_{Co^{2+}|Co} = -0.28 \text{ V}$, $E^{\odot}_{\text{Cu}^{2+}|\text{Cu}} = +0.34 \text{ V}, E^{\odot}_{\text{Zn}^{2+}|\text{Zn}} = -0.76 \text{ V}$

Which metal will corrode fastest?

- (2) Cu
- (3) Co
- 19. Red hot carbon will remove oxygen from the oxides XO and YO but not from ZO. Y will remove oxygen from XO. Use this evidence to deduce the order of activity of the three metals X, Y, and Z, putting the most reactive first.
 - (1) X, Y, Z (2) Z, Y, X
- (3) Y, X, Z
- (4) Z, X, Y
- 20. Among Na, Hg, S, Pt, and graphite which can be used as electrodes in electrolytic cell having aqueous solutions?
 - (1) Na and S
- (2) Hg, Pt, and S
- (3) Na, Hg, and S
- (4) Hg, Pt, and graphite

- 21. In an electrolytic cell current flows
 - (1) From cathode to anode in outer circuit
 - (2) From anode to cathode outside the cell
 - (3) From cathode to anode inside the cell
 - (4) None of the above
- (4) None of the ass.

 22. The reaction $Cu^{2+}(aq) + 2Cl^{\Theta}(aq) \longrightarrow Cu(s) + Cl_{2}(g) h_{dg}$ $E_{\text{cell}}^{\ominus} = -1.03 \text{ V. This reaction}$
 - (1) Can be made to produce electricity in voltaic cell
 - (2) Can be made to occur in an electrolytic cell
 - (3) Can occur in acidic medium only
 - (4) Can occur in basic medium only
- 23. Which statement is true about a spontaneous cell reaction in galvanic cell?
 - (1) $E_{\text{cell}}^{\ominus} > 0$; $\Delta G^{\ominus} < 0$; Quotient $Q < K_c$
 - (2) $E_{\text{cell}}^{\ominus} < 0$; $\Delta G^{\ominus} > 0$; $Q < K_{\text{c}}$
 - (3) $E_{\text{cell}}^{\ominus} > 0$; $\Delta G^{\ominus} > 0$; $Q > K_{c}$
 - (4) $E_{\text{cell}}^{\ominus} > 0$; $\Delta G^{\ominus} > 0$; $Q < K_{c}$
- 24. Zn acts as sacrificial or cathodic protect ion to prevent rusting of iron because
 - (1) E^{\odot}_{OP} of $Zn < E^{\odot}_{OP}$ of Fe
 - (2) E^{\ominus}_{OP} of $Zn > E^{\ominus}_{OP}$ of Fe
 - (3) E^{\ominus}_{OP} of $Zn = E^{\ominus}_{OP}$ of Fe
 - (4) Zn is cheaper than iron
- 25. The oxidation potential of a hydrogen electrode at pH = 10and $p_{\rm H_2} = 1$ atm is
 - (1) -0.59 V (2) 0.00 V (3) +0.59 V (4) 0.059 V
- **26.** E^{\odot} of Mg²⁺ | Mg, Zn⁺² | Zn, and Fe²⁺ | Fe are -2.37 V. -0.76 V, and -0.44 V, respectively. Which of the following is correct?
 - (1) Mg oxidizes Fe
- (2) Zn oxidizes Fe
- (3) Zn reduces Mg²⁺
- (4) Zn reduces Fe²⁺
- 27. The solution of CuSO₄ in which copper rod is immersed is diluted to 10 times. The reduction electrode potential
 - (1) Increases by 30 mV
- (2) Decreases by 30 mV
- (3) Increases by 59 mV
- (4) Decreases by 59 mV
- **28.** Deduce from the following E^{\odot} values of half cells, what combination of two half cells would results in a cell with the largest potential?
 - I. $A + e^- \longrightarrow A^{\odot}$.

- $E^{\Theta} = -0.24 \text{ V}$ $E^{\odot} = +1.25 \text{ V}$
- II. $B^{\odot} + e^{-} \longrightarrow B^{2-}$ III.C $^{\odot}$ + 2 $e^ \longrightarrow$ C $^{3-}$
- $E^{\Theta} = -1.25$
- IV. D + $2e^- \longrightarrow D^{2-}$
- $E^{\Theta} = +0.68 \,\mathrm{V}$
- (1) II, IV (2) II, III
- (3) III, IV
- (4) I, II
- **29.** Given that $E^{\odot}_{\text{Fe}^{2+}|\text{Fe}} = -0.44 \text{ V}; E^{\odot}_{\text{Fe}^{2+}|\text{Fe}^{3+}} = -0.77 \text{ V}$ If Fe²⁺, Fe³⁺ and Fe solid are kept together, then
 - (1) Fe³⁺ increases
 - (2) Fe³⁺ decreases
 - (3) Fe²⁺, Fe³⁺ remain unchanged
 - (4) Fe²⁺ decreases
- 30. A galvanic cell is set up from a zinc bar weighing 100 g and 1.0 L of 1.0 M CuSO₄ solution. How long would

	deliver a steady current of				
	the cell run if it is assumed to deliver a steady current of 1.0 A. (Atomic mass of $Zn = 65$)				
	thermodynamic efficiency of cell is given by				
	(1) $\Delta H/\Delta G$ (2) $\frac{m E}{\Delta G}$ (3) $\frac{m}{\Delta H}$ (4) nFE^{\odot}				
	$A(s) + 2B^{\oplus} \longrightarrow A^{2+} + 2B$				
32.	. Loop follow to be to a fine L and its				
	264 M (2) 0 708 V (3) 0.0098 V (4) 1.30 V				
	will the reduction potential of a nydrogen				
33.	electrode change when its solution initially at par				
	$\frac{1}{2}$ = $\frac{1}{2}$ = $\frac{1}{2}$				
	(1) Increase by 0.059 V (2) Decrease by 0.059 V				
	(3) Increase by 0.41 V (4) Decrease by 0.41 V				
34.	If $E^{\odot}_{\text{Fe}^{3+} \text{Fe}}$ and $E^{\odot}_{\text{Fe}^{2+} \text{Fe}}$ are -0.36 V and -0.439 V ,				
	respectively, then the value of $E_{\text{Fe}^{3+} \text{Fe}^{2+} \text{S}}^{2+}$				
	(1) (-36 – 0.439) V				
	(2) $[3(-0.36) + 2(-0.439)]$ V				
	(3) (-0.36 - 0.439) V				
	(4) [3(-0.36) – 2 (-0.439)] V				
35.	The standard electrode potential of a metal ion $(Ag \mid Ag^{\oplus})$ and metal-insoluble salt anion $(Ag \mid AgCl \mid Cl^{\odot})$ are related				
	as RT				
	$(1) E^{\ominus}_{Ag^{\bigoplus} \mid Ag} = E^{\ominus}_{Cl^{\ominus} \mid AgCl \mid Ag} + \frac{RT}{F} \ln K_{sp}$				
	$(2) E^{\ominus}_{\text{Cl}^{\ominus} \text{AgCl} \text{Ag}} = E^{\ominus}_{\text{Ag} \oplus \text{Ag}} + \frac{RT}{F} \ln K_{\text{sp}}$				
	(3) $E^{\ominus}_{Ag^{\bigoplus} Ag} = E^{\ominus}_{Cl^{\ominus} AgCl Ag} + \frac{RT}{F} \ln \frac{[Cl^{\ominus}]}{K_{sp}}$				
	(4) $E^{\ominus}_{\text{Cl}^{\ominus} \mid \text{AgCl} \mid \text{Ag}} = E^{\ominus}_{\text{Ag}^{\oplus} \mid \text{Ag}} + \frac{RT}{F} \ln \frac{K_{\text{sp}}}{[\text{Cl}^{\ominus}]}$				
36	. The standard reduction potential at 25°C for the reaction,				
	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH \text{ is } -0.8277 \text{ volt. The}$				
	equilibrium constant for the reaction:				
	$2H_2O \Longrightarrow H_3O^{\oplus} + \stackrel{\odot}{OH}$ at 25°C is				
	(1) 10^{-12} (2) 10^{-14} (3) 10^{-11} (4) 10^{-8}				
37	• What would be the magnitude of the EMF of the following cell:				
	$Pt(H_2)$ 0.1 M acetic acid 0.1 M formic acid $Pt(H_2)$				

at 25°C? The ionization constant of acetic acid, $K_a \sim 10^{-5}$,

(1) 0.0295 V (2) 0.059 V (3) -0.059 V (4) -0.0295 V38. In an experiment set up for the measurement of EMF of a

half cell using a reference electrode and a salt bridge, when

while that of formic acid, $K_a \sim 10^{-4}$.

the salt bridge is removed, the voltage

(1) Does not change

calomel electrode (with electrode potential = 0.28 V) is (4) 0.218(3) 0.332(2) 0.664(1) 0.10444. The potential of a hydrogen electrode in a solution with pH = 5 at $25^{\circ}C$ is (4) 0.295(3) -0.295(2) - 0.59(1) + 0.5945. The potential of a hydrogen electrode in a solution with pOH = 4 at $25^{\circ}C$ is (3) -0.59(4) 0.59(2) 0.059(1) -0.059**46.** Consider the electrode Ag | AgCl(s), Cl[©] (0.1 M), i.e., silver electrode in contact with 0.1 M KCl solution saturated with AgCl. If it is combined with the electrode Ag \mid Ag $^{\oplus}$ (0.1 M) to form a complete cell, the EMF would be $(K_{\rm sp} \text{ of AgCl} = 10^{-10} \text{ at } 25^{\circ}\text{C})$ (4) 0.472(3) 0.59(1) 0.799(2) 0.63647. The standard EMF of decinormal calomel electrode is 0.268 V. The EMF is (1) -0.298 V (2) 0.327 V (3) -0.327 V (4) 0.298 V 48. The standard EMF of quinhydrone electrode is 0.699 V. The EMF of the quinhydrone electrode dipped in a solution with pH = 10 is(2) -0.109 V(1) 0.109 V (4) - 1.289 V(3) 1.289 V 49. A hydrogen electrode placed in a solution containing sodium acetate and acetic acid in the ratio of x : y and y : x has an electrode potential value E_1 and E_2 volts, respectively, at 25°C. The pK_a value of acetic acid is $(1) \; \frac{-(E_1 + E_2)}{2 \times 0.059}$ $(4) \ \frac{-(E_1 + E_2)}{0.059}$ $(3) \ \frac{E_2 - E_1}{2 \times 0.059}$

(2) Increases to maximum

(4) Drops to zero

following?

(1) ZnCl₂

(1) Na[⊕]

(3) Decreases to half the value

strongest oxidizing agent?

(2) Li[⊕]

39. The reference calomel electrode is made from which of the

(2) $CuSO_4$ (3) Hg_2Cl_2

40. The standard reduction potential of $Li^{\oplus} \mid Li$, $Ba^{2+} \mid Ba$, Na^{\oplus} | Na and Mg^{2+} | Mg are -3.05, -2.73, -2.71, and -2.37 volts, respectively. Which one of the following is the

41. What is the electrode potential of a gaseous hydrogen electrode dipped in a solution pH = 5.0 relative to the calomel electrode with an electrode potential of +0.28 V? (1) -0.015 V (2) +0.575 V (3) +0.015 V (4) -0.575 V42. The EMF of a concentration cell consisting of two zinc electrodes, one dipping into M/4 solution of ZnSO₄ and the

other into M/16 solution of the same salt at 25°C is (1) 0.0125 V (2) 0.0250 V (3) 0.0178 V (4) 0.0356 V43. A certain electrode has standard (reduction potential) of 0.384 V. The potential when measured against a normal

(4) HgCl₂

(3) Ba^{2+} (4) Mg^{2+}

50. Given standard E^{\odot} :

$$Fe^{3+} + 3e^{-} \longrightarrow Fe;$$

$$E^{\odot} = -0.036 \text{ V}$$

$$Fe^{2+} + 2e^{-} \longrightarrow Fe$$
;

$$E^{\odot} = -0.440 \text{ V}$$

The
$$E^{\odot}$$
 of $Fe^{3+} + e^{-} \longrightarrow Fe^{2+}$ is

(1)
$$-0.476 \text{ V}$$
 (2) -0.404 V (3) 0.404 V (4) 0.772 V

- 51. For the cell $Zn(s) \mid Zn^{2+} \mid Cu^{2+} \mid Cu(s)$, the standard cell voltage, E_{cell}° is 1.10 V. When a cell using these reagents was prepared in the lab, the measured cell voltage was 0.98 V . One possible explanation for the observed voltage is
 - (1) There were 2.00 mol of Zn^{2+} but only 1.00 mol of Cu^{2+} .
 - (2) The Zn electrode had twice the surface of the Cu electrode.
 - (3) The $[Zn^{2+}]$ was larger than the $[Cu^{2+}]$.
 - (4) The volume of the Zn²⁺ solution was larger than the volume of the Cu²⁺ solution.
- **52.** $\Delta G = \Delta H T \Delta S$ and

$$\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT} \right]_P$$
, then $\left(\frac{dE_{\text{cell}}}{dT} \right)$ is

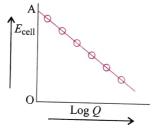
- (1) $\frac{\Delta S}{nF}$ (2) $\frac{nE}{\Delta S}$ (3) $-nFE_{\text{cell}}$ (4) nFE_{cell}
- 53. $Zn + Cu^{2+}(aq) \rightleftharpoons Cu + Zn^{2+}(aq)$.

Reaction quotient is $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$. Variation of E_{cell} with $\log Q$

is of the type with OA = 1.10 V.

 $E_{\rm cell}$ will be 1.1591 V when

- (1) $[Cu^{2+}] / [Zn^{2+}] = 0.01$
- (2) $[Zn^{2+}] / [Cu^{2+}] = 0.01$.
- (3) $[Zn^{2+}] / [Cu^{2+}] = 0.1$
- (4) $[Zn^{2+}] / [Cu^{2+}] = 1$



54. $Cu^{\oplus} + e^{-} \longrightarrow Cu, E^{\ominus} = x_1 \text{ volt}$

$$Cu^{2+} + 2e^{-} \longrightarrow Cu, E^{\odot} = x_2 \text{ volt, then for}$$

$$Cu^{2+} + e^{-} \longrightarrow Cu^{\oplus}, E^{\ominus}(\text{volt}) \text{ will be}$$

- (1) $x_1 2x_2$ (2) $x_1 + 2x_2$ (3) $x_1 x_2$ (4) $2x_2 x_1$
- **55.** $\operatorname{Zn} | \operatorname{Zn^{2+}}(c_1) || \operatorname{Zn^{2+}}(c_2) | \operatorname{Zn}$. For this cell ΔG is negative if:
 - (1) $c_1 = c_2$ (2) $c_1 > c_2$ (3) $c_2 > c_1$
- (4) None
- **56.** Pt $|(H_2)(p_1)| H^{\oplus}(1 M)|(H_2)(p_2)|$ Pt cell reaction will be exergonic if
 - $(1) p_1 = p_2$
- (2) $p_1 > p_2$
- $(3) p_2 > p_1$
- (4) $p_1 = 1$ atm
- 57. $Pt|(Cl_2)(p_1)|HCl(0.1 M)|(Cl_2)(p_2)|Pt cell reaction will$ be endergonic if
 - $(1) p_1 = p_2$
- (2) $p_1 > p_2$
- $(3) p_2 > p_1$
- (4) $p_1 = p_2 = 1$ atm
- 58. $Pt|(H_2)$ (1 atm) | H_2O , electrode potential at 298 K is
 - (1) -0.2364 V
- (2) -0.4137 V
- (3) 0.4137 V
- (4) 0.00 V

59. For the half cell

OH
OH
OH
$$+2H^{\oplus}+2e^{-}, E^{\ominus}=1.30 \text{ V}$$

At pH = 2, the electrode potential is

- (1) 1.36 V
- (2) 1.30 V
- (3) 1.42 V
- (4) 1.20 V
- 60. Which of the following changes will increase the EMF of the cell: $Co(s) \mid CoCl_2(M_1) \parallel HCl(M_2) (H_2, g) Pt?$
 - (1) Increase in the volume of $CoCl_2$ solution from 100 mto 200 mL.
 - (2) Increase M_2 from 0.01 M to 0.50 M.
 - (3) Increase the pressure of the $H_2(g)$ from 1.00 to 2.00 atm
 - (4) Increase M_1 from 0.01 to 0.50 M.
- **61.** Ag $|Ag^{\oplus}(1 M) ||Ag^{\oplus}||Ag$
 - 1 L solution

1 L solution

- $0.5\ F$ electricity in the LHS (anode) and $1\ F$ of electricity in the RHS (cathode) is first passed making them independent electrolytic cells at 298 K. EMF of the cell after electrolysis will be
- (1) Increased
- (2) Decreased
- (3) No change
- (4) Time is also required
- 62. The cell EMF is independent of the concentration of the species of the cell in
 - (1) Fe $\stackrel{\frown}{+}$ FeO(s) | KOH(aq) | NiO(s) | Ni₂O₃(s) | Ni
 - (2) Pt | (H₂) | HCl | (Cl₂) Pt
 - (3) $Zn | Zn^{2+} || Cu^{2+} | Cu$
 - (4) Hg , $\operatorname{Hg}_2\operatorname{Cl}_2 | \operatorname{KCl} | \operatorname{AgNO}_3 | \operatorname{Ag}$
- 63. Given the standard potential of the following at 25°C.

$$MnO_2 \longrightarrow Mn^{3+};$$

 $F^{\odot} = 0.95 \text{ V}$ $E^{\Theta} = 1.51 \text{ V}$

 $Mn^{3+} \longrightarrow Mn^{2+}$;

The standard potential of $MnO_2 \longrightarrow Mn^{2+}$ is

- (1) -0.56 V (2) -2.46 V (3) -1.23 V (4) 1.23 V**64.** The potential of the following cell at 25°C is
 - $\Pr\left|\frac{H_2}{(1 \text{ atm})} \left|\frac{HNO_3}{(0.1 \text{ M})} \right| \frac{NaOH}{(10^{-3} \text{ M})} \left|\frac{H_2}{(1 \text{ atm})} \right| \Pr\left|\frac{H_2}{(1 \text{ atm})} \right| \right|$
 - (1) -0.059 V (2) 0.059 V (3) -0.59 V (4) 0.5 V
- 65. Given the following cell at 25°C

$$Pt = H_2 | CH_3COOH | NaOH | H_2 | (10^{-3}M) | (10^{-3}M) | (1atm) | Pt.$$

What will be the potential of the cell?

Given pK_a of $CH_3COOH = 4.74$

- (1) -0.42 V (2) 0.42 V
- (3) -0.19 V (4) 0.19 V
- 66. What is the potential of the cell containing two hydrogen electrodes as represented below?

$$P_{t}; \frac{1}{2}H_{2}(g) | H_{2}O | H_{0}^{\oplus}(0.001 M) | 1/2H_{2}(g) P_{t}$$

- (1) -0.236 V
- (2) -0.0591 V
- (3) 0.236 V
- (4) 0.0591 V
- 67. Given electrode potentials are

$$Fe^{3+} + e^- \longrightarrow Fe^{2+};$$

$$E^{\odot} = 0.771 \text{ V}$$

$$I_1 + 2e^- \longrightarrow 2I^{\odot};$$

$$E^{\odot} = 0.536 \text{ V}$$

 E^{\odot}_{cell} for the cell reaction,

$$2Fe^{3+} + 2I^{\odot} \longrightarrow Fe^{2+} + I_2$$
 is

$$(1) (2 \times 0.771 - 0.536) = 1.006 \text{ V}$$

$$(2)(0.771 - 0.5 \times 0.536) = 0.503 \text{ V}$$

$$(3)(0.771 - 0.536) = 0.235 \text{ V}$$

$$(4)(0.536 - 0.771) = -0.236 \text{ V}$$

68. The following facts are available:

$$2A^{\odot} + B_2 \longrightarrow 2B^{\odot} + A_2;$$

 $2C^{\ominus} + B_2 \longrightarrow \text{No reaction};$

$$2D^{\ominus} + A_2 \longrightarrow 2A^{\ominus} + D_2$$

Which of the following statement is correct?

- $(1)\,E^{\ominus}_{C^{\ominus}\,|\,C_{2}}\!\!>\!E^{\ominus}_{B^{\ominus}\,|\,B_{2}}\!\!>\!E^{\ominus}_{A^{\ominus}\,|\,A_{2}}\!\!>\!E^{\ominus}_{D^{\ominus}\,|\,D_{2}}$
- $(2)\,E^{\ominus}_{C^{\ominus}\,|\,C_{2}}\!\!<\!E^{\ominus}_{B^{\ominus}\,|\,B_{2}}\!\!<\!E^{\ominus}_{A^{\ominus}\,|\,A_{2}}\!\!<\!E^{\ominus}_{D^{\ominus}\,|\,D_{2}}$
- ${}^{(3)}E^{\ominus}_{C^{\ominus}\mid C_{2}} < E^{\ominus}_{B^{\ominus}\mid B_{2}} > E^{\ominus}_{A^{\ominus}\mid A_{2}} > E^{\ominus}_{D^{\ominus}\mid D_{2}}$
- $(4) E^{\ominus}_{C^{\ominus} \mid C_{2}} > E^{\ominus}_{B^{\ominus} \mid B_{2}} < E^{\ominus}_{A^{\ominus} \mid A_{2}} < E^{\ominus}_{D^{\ominus} \mid D_{2}}$
- 69. The potential of the cell at 25° C is

$$\Pr \left| \frac{H_2}{(1 \text{ atm})} \right| \frac{NH_4OH}{(10^{-3} \text{M})} \left| \frac{NaOH}{(10^{-3} \text{M})} \right| \frac{H_2}{(1 \text{ atm})} \right| \Pr$$

Given pK_h of $NH_4OH = 4.74$

- (1) 0.05 V (2) -0.05 V (3) -0.28 V (4) 0.28 V
- 70. The potential of the cell at 25°C is

Given pK_a of CH_3COOH and pK_b of $NH_4OH = 4.74$

- (1) -0.04 V (2) 0.04 V (3) -0.189 V (4) 0.189 V
- 71. Calculate the potential of the following cell:

$$\begin{array}{c|c}
Pt & Co^{2+}, Co^{3+} & Cr^{3+}, Cr_2O_7^{2-}, H^{\oplus} \\
(2.0 \text{ M}) (1.0 \text{ M}) & (1.0 \text{ M}) (4.0 \text{ M}) (1.0 \text{ M})
\end{array} Pt$$

$$E^{\odot}_{\text{Co}^{2+}|\text{Co}^{3+}} = -2\text{V}, E^{\odot}_{\text{Cr}_2\text{O}_7^{2-}|\text{Cr}^{3+}} = +1.0\text{ V}$$

- (1) 1.024 V (2) -1.024 V (3) 0.976 V (4) -0.976 V
- 72. If $Fe^{3+} + Y^{4-} \rightleftharpoons FeY^{\odot}$;
- $K = 1.3 \times 10^{25}$
- $Fe^{2+} + Y^{4-} \Longrightarrow FeY^{2-}$;
- $K = 2.1 \times 10^{14}$

- $Fe^{3+} + e^- \Longrightarrow Fe^{2+}$ $E^{\odot} = +0.77 \text{ V}$ E^{\odot} for FeY $^{\odot}$ + e^{-} \longrightarrow FeY $^{2-}$
- (1) 0.13 V (2) -0.636 V (3) +0.636 V (4) 1.41 V
- 73. Calculate E^{\odot} for the reactions:

 $ZnY^{2-} + 2e^{-} \rightleftharpoons Zn(s) + Y^{4-}$, where Y^{4-} is the completely deprotonated anion of EDTA. The formation constant for ZnY^{2-} is 3.2×10^{16} and E^{\odot} for $Zn \longrightarrow Zn^{2+} + 2e^{-}$ is 0.76 V.

- (1) -1.25 V (2) 0.48 V (3) +0.68 V (4) -0.27 V
- 74. The solubility product of Pb₃(AsO₄)₂ is 4.1×10^{-36} . E^{\odot} for the reaction:

$$Pb_3(AsO_4)_2(s) + 6e^- \iff 3Pb(s) + 2AsO_4^{2-} \text{ if}$$

 $E_{Pb^{2+}|Pb}^{\ominus} = -0.13 \text{ V}$

- (1) $\pm 0.478 \text{ V}$ (2) $\pm 0.13 \text{ V}$ (3) $\pm 0.478 \text{ V}$ (4) $\pm 0.13 \text{ V}$
- 75. A cell is to be constructed to show a redox change: $Cr + 2Cr^{3+} \Longrightarrow 3Cr^{2+}$. The number of cells with different E^{\odot} and n but same value of ΔG^{\odot} can be made (Given $E^{\odot}_{\text{Cr}^{3+}|\text{Cr}^{2+}} = -0.40 \text{ V}, E^{\odot}_{\text{Cr}^{3+}|\text{Cr}} = -0.74 \text{ V}, \text{ and } E^{\odot}_{\text{Cr}^{2+}|\text{Cr}}$ =-0.91 V
 - (1) 1(2) 2(3) 3
- 76. E^{\odot} for $Cr^{3+} + 3e^{-} \longrightarrow Cr$ and $Cr^{3+} + e^{-} \longrightarrow Cr^{2+}$ are -0.74 V and -0.40 V, respectively. E^{\odot} for the reaction is $Cr^{+2} + 2e^{-} \longrightarrow Cr$
 - (1) -0.91 V (2) +0.91 V (3) -1.14 V (4) +0.34 V
- 77. The efficiency of a fuel cell is 80% and the standard heat of reaction is -300 kJ. The reaction involves two electrons in redox change. E^{\odot} for the cell is
 - (1) 1.24 V (2) 2.48 V (3) 0 V
- 78. The $E_{\rm cell}$ for a given cell is 1.2346 and 1.2340 V at 300 K and 310 K, respectively. Calculate the change in entropy during the cell reaction if the redox change involves three electrons.
 - $(1) -17.37 \text{ J K}^{-1}$
- $(2) + 17.37 \text{ J K}^{-1}$
- (3) 173.7 J K^{-1}
- (4) 5.79 J K^{-1}
- **79.** The E^{\odot} for Cu^{2+}/Cu^{\oplus} , Cu^{\oplus}/Cu , Cu^{2+}/Cu , are 0.15 V, 0.50 V, and 0.325 V, respectively. The redox cell showing redox reaction $2Cu^{\oplus} \longrightarrow Cu^{2+} + Cu$ is made. E^{\odot} of this cell reaction and ΔG^{\odot} may be
 - (1) $E^{\odot} = 0.175 \text{ V or } E^{\odot} = 0.350 \text{ V}$
 - (2) n = 1 or 2
 - (3) $\Delta G^{\odot} = -33.775 \text{ k}$
 - (4) All of these
- **80.** For the given cell $Pt_{D_{2}|D^{\oplus}} || H^{\oplus} | Pt_{H_{2}}$, if $E^{\ominus}_{D_{2}|D^{\oplus}} = 0.003 \text{ V}$, what will be the ratio of D[⊕] and H[⊕] at 25°C when the reaction $D_2 + 2H^{\oplus} \longrightarrow 2D^{\oplus} + H_2$ attains equilibrium
 - (1) 1.34 (2) 1.24
- (3) 1.124
- (4) 1.45
- **81.** What is E°_{red} for the reaction: $Cu^{2+} + 2e^{-} \longrightarrow Cu$ in the half cell $\operatorname{Pt}_{\operatorname{S}^2 \cap \operatorname{CuS} + \operatorname{Cu}}$ if $E^{\odot}_{\operatorname{Cu}^{2+} + \operatorname{Cu}}$ is 0.34 V and K_{sp} of $CuS = 10^{-35}$?
 - (1) 0.34 V
- (2) -0.6925 V
- (3) +0.6925 V
- (4) -0.66 V

82. A half cell reaction $Ag_2S(s) + 2e^- \longrightarrow 3Ag(s) + S^{2-}$ is carried out in a half cell $Pt_{Ag_2S \mid Ag, H_2S (0.1 \text{ M})}$, at $[H^{\oplus}] = 10^{-3}$. The EMF of the half cell is

The EMF of the half cert is
$$[E^{\odot}_{Ag^{\oplus}|Ag} = 0.80 \text{ V}, K_{a(H_2S)} = 10^{-21}, \text{ and } K_{sp} \text{ of } Ag_2S = 10^{-49}]$$

- (1) -0.1735 V
- (3) +0.1735 V
- (4) +0.19 V
- 83. The calomel and quinhydrone electrodes are reversible with respect to which ions, respectively?
 - (1) Cl[⊙], H[⊕]
- (2) H[⊕], Cl[⊙]
- $(3) \text{ Hg}_{2}^{2+}, \text{ OH}$
- (4) Hg_2^{2+} , H^{\oplus}
- **84.** The electrode with reaction: $\operatorname{Cr}_2\operatorname{O}_7^{2-}(\operatorname{aq}) + 14\operatorname{H}^{\oplus}(\operatorname{aq})$ $+6e^{-} \longrightarrow 2Cr^{3+}(aq) + 7H_2O$ can be represented as
 - (1) Pt | $H^{\oplus}(aq)$, $Cr_2O_7^{2-}(aq)$
 - (2) Pt $\mid H^{\oplus}(aq), Cr_2O_7^{2-}(aq), Cr_3^{3+}(aq)$
 - (3) Pt $|H_2| H^{\oplus}(aq)$, $Cr_2O_7^{2-}$
 - (4) Pt $|H_2|$ H^{\oplus}(aq), Cr₂O₇²⁻(aq), Cr³⁺(aq)
- 85. For a given reaction: $M^{(x+n)} + ne^- \longrightarrow M^{x+}$, E_{red}^{\ominus} is known along with M^{x+n} and M^{x+1} ion concentrations. Then
 - (1) n can be evaluated
 - (2) x can be evaluated
 - (3) (x + n) can be evaluated
 - (4) n, x, (x + n) can be evaluated
- 86. From the following information, calculate the solubility product of AgBr.

$$AgBr(s) + e^{-} \longrightarrow Ag(s) + Br^{\ominus}(aq);$$

$$E^{\odot} = 0.07 \text{ V}$$

$$Ag^{\oplus}(aq) + e^{-} \longrightarrow Ag(s);$$

$$E^{\odot} = 0.80 \text{ V}$$

(1)
$$4 \times 10^{-13}$$
 (2) 4×10^{-10} (3) 4×10^{-17} (4) 4×10^{-7}

87. Suppose that gold is being plated onto another metal in a electrolytic cell. The half-cell reaction producing the Au(s) is $\operatorname{AuCl}_{\Delta}^{\ominus} \longrightarrow \operatorname{Au}(s) + 4\operatorname{Cl}^{\ominus} + 3e^{-}$

If a 0.30-A current runs for 1.50 min, what mass of Au(s) will be plated, assuming all the electrons are used in the reduction of AuCl₄[⊙]?

- (1) 0.184 g (2) 0.551 g (3) 1.84 g
- 88. What is the cell entropy change (in $J K^{-1}$) of the following cell?

$$Pt(s) \begin{vmatrix} H_2(g) \\ p = 1 \text{ atm} \end{vmatrix} CH_3COOH, HCI \begin{vmatrix} KCl (aq) \\ 0.1 \text{ M} \end{vmatrix} Bg_2Cl_2(s) Hg$$

The EMF of the cell is found to be 0.045 V at 298 K and temperature coefficient is $3.4 \times 10^{-4} \text{ V K}^{-1}$.

(Given: $K_{a(CH_3COOH)} = 10^{-5} \text{ M}$) (1) 60 (2) 65.2 (3) 69.2

- (4)63.5
- **89.** ΔG^{\odot} of the reaction is:

$$4Al + 3O_2 + 6H_2O + 4OH \longrightarrow 4Al(OH)_4^{\odot}$$

 $E_{cell}^{\odot} = 2.73 \text{ V}$

$$\Delta_{\rm f} G^{\odot}_{\rm (OH)}^{\odot} = -157 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} G^{\odot}_{\rm (H_2O)} = -237 \text{ kJ mol}^{-1}$$

- $(1) -3.16 \times 10^3 \text{ kJ mol}^{-1}$ (2) $-0.79 \times 10^3 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$
- (3) $-0.263 \times 10^3 \text{ kJ mol}^{-1}$ (4) $+0.263 \times 10^3 \text{ kJ mol}^{-1}$
- 90. $Cu^{2+} + 2e^{-} \longrightarrow Cu$. For this, graph between EIn[Cu²⁺] is a straight line of intercept 0.34 V, then the electrode oxidation potential of the half cell $Cu \mid Cu^{2+}$ (0.1 M) will be

 - (1) $0.34 + \frac{0.0591}{2}$ (2) $-0.34 \frac{0.0591}{2}$
 - (3) 0.34
- $(4) -0.34 + \frac{0.0591}{2}$
- 91. A cell Cu | Cu²⁺ || Ag^{\oplus} | Ag initially contains 2 M Ag^{\oplus} and 2 M Cu²⁺ ions in 1 L solution each. The change in cell potential after it has supplied 1 A current for 96500 s is
 - (1) -0.003 V
- (2) -0.02 V
- (3) -0.04 V
- (4) None of these
- **92.** The value of the reaction quotient Q for the cell $Zn(s) \mid Zn^{2+} (0.01 \text{ M}) \parallel Ag^{\oplus} (1.25 \text{ M}) \mid Ag(s) \text{ is}$
 - (1)156

- (2) 125
- $(3) 1.25 \times 10^{-2}$
- $(4) 64 \times 10^{-3}$
- **93.** In acid medium, MnO_4^{\odot} is an oxidizing agent.

$$\mathrm{MnO_4}^{\ominus} + 8\mathrm{H}^{\oplus} + 5e^- \longrightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}$$

If H[⊕] ion concentration is doubled, electrode potential of the half cell MnO₄[⊙], Mn²⁺ | Pt will

- (1) Increase by 28.36 mV (2) Decrease by 28.36 mV
- (3) Increase by 14.23 mV (4) Decrease by 142.30 mV
- **94.** A reaction:

$$\frac{1}{2}H_2(g) + AgCl(s) \iff H^{\oplus}(aq) + Cl^{\Theta}(aq) + Ag(s)$$

occurs in a galvanic cell. The structure of the cell will be

- (1) Ag, AgCl(s) | KCl(sol) | AgNO₃(sol), Ag
- (2) Pt, $H_2(g) \mid HCl(sol) \mid AgNO_3(sol)$, Ag
- (3) Pt, $H_2(g) \mid HCl(sol) \mid AgCl(s)$, Ag
- (4) Pt, $H_2(g)$ | KCl(sol) | AgCl(s), Ag
- **95.** If the temperature coefficient of EMF is -0.125 V K^{-1} . ΔS for the given cell at 25°C is:

Fe | Fe²⁺(aq) || Cd²⁺(aq) | Cd

- $(1) -26.125 \text{ kJ K}^{-1}$
- (2) -24.125 kJ K⁻¹
- (3) $-22.125 kJ K^{-1}$
- $(4) -20.125 \text{ kJ K}^{-1}$
- 96. Which of the following is(are) function(s) of salt bridge?
 - (1) It completes the electrical circuit with electrons flowing from one electrode to other through wires and flow of ions between the two compartments through salt bridge.
 - (2) It prevents the accumulation of the ions.
 - (3) Both (1) and (2).
 - (4) None of the above.
- 97. $Cu^{2+} + 2e^{-} \longrightarrow Cu$. On increasing $[Cu^{2+}]$, electrode potential
 - (1) Increases

- (2) Decreases
- (3) No change
- (4) First increases, then decreases
- 98. The standard electrode potentials of Fe^{2+} | Fe and Sn²⁺ | Sn electrodes are -0.44 and -0.14 V, respectively. For the reaction Fe + $Sn^{2+} \longrightarrow Fe^{2+} + Sn$

The standard EMF is:

- (1) -0.58 V
- (2) -0.30 V
- (3) +0.30 V
- (4) +0.58 V
- 99. The standard reduction potentials at 298 K are given against each of the following half cell reactions:
 - I. $E^{\odot}_{Zn^{2+}|Zn} = -0.76 \text{ V}$
- II. $E^{\odot}_{\text{Cr}^{3+}|\text{Cr}} = -0.74 \text{ V}$
- III. $E^{\ominus}_{H^{\bigoplus}|H_{2}} = 0.00 \text{ V}$ IV. $E^{\ominus}_{Fe^{3+}|Fe^{+2}} = +0.77 \text{ V}$

Based on the above data, state which of the following is the strongest reducing agent?

- (1) Zn
- (2) Cr
- $(3) H_{2}$
- (4) Fe
- 100. For hydrogen-oxygen fuel cell with reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

 $\Delta G_f^{\odot}(H_2O) = -237.2 \text{ kJ mol}^{-1}$. Hence, EMF of the fuel cell is

- (1) + 2.46 V
- (2) 2.46 V
- (3) + 1.23 V
- (4) 1.23 V
- 101. A metal-insoluble salt electrode consists of
 - (1) A piece of metal placed in a solution containing a sparingly soluble salt.
 - (2) Crystals of an insoluble salt coated with a metal.
 - (3) A piece of metal coated with one of its insoluble salts.
 - (4) A metal fixed with an insoluble salt at high temperature.
- 102. Which of the following is the most powerful reducing agent?
 - (1) F[⊙]
- (2) C1[©]
- (3) Br[⊙]
- (4) I[⊙]
- 103. If all species are in their standard states, which of the following is the strongest oxidizing agent?
 - (1) Br⁽³⁾
- $(2) Zn^{2+}$
- $(3) \text{ Co}^{3+}$
- $(4) \text{ Fe}^{2+}$
- 104. The standard EMF of a galvanic cell involving cell reaction with n = 2 is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be
 - (1) 4.0×10^{12}
- $(2) 1.0 \times 10^2$
- (3) 1.0×10^{10}
- $(4)\ 2.0 \times 10^{11}$
- 105. The correct order of reactivity of K, Mg, Zn, and Cu with water according to the electrochemical series is
 - (1) K > Mg > Zn > Cu
- (2) Mg > Zn > Cu > K
- (3) $K > Z_n > M_g > Cu$
- (4) Cu > Zn > Mg > K
- 106. If $E^{\ominus}_{Fe^{2+}|Fe}$ is x_1 , $E^{\ominus}_{Fe^{3+}|Fe}$ is x_2 , then $E^{\ominus}_{Fe^{3+}|Fe^{2+}}$ will be
 - (1) $3x_2 2x_1$
- $(2) x_2 x_1$
- $(3) x_2 + x_1$ $(4) 2x_2 + 3x_2$

- **107.** For Pt | $Cl_2(p_1)$ | HCl (0.1 M) | $Cl_2(p_2)$ | Pt, cell reaction will be spontaneous if
 - $(1) p_1 = p_2$
- $(2) p_1 > p_2$
- $(3) p_2 > p_1$
- (4) $p_1 = 1$ atm
- 108. Consider the following cell with hydrogen electrodes at different pressure p_1 and p_2 .

Pt,
$$H_2(p_1) \mid H^{\oplus}(aq) \mid H_2(p_2)$$
, Pt 1 M

The EMF of the cell is given by

- $(1) \frac{RT}{F} \ln \frac{p_1}{p_2}$
- $(2) \frac{RT}{2F} \ln \frac{p_1}{p_2}$
- $(3) \frac{RT}{F} \ln \frac{P_2}{P_1}$
- $(4) \frac{RT}{2F} \ln \frac{p_2}{p_1}$
- 109. Consider the cell given below:

$$Ag(s) \mid Ag^{\oplus .} \parallel Cu^{2^+} \mid Cu(s)$$

$$Ag^{\oplus} + e^{-} \longrightarrow Ag; E^{\ominus} = x$$

$$Cu^{2+} + 2e^{-} \longrightarrow Cu; E^{\Theta} = y$$

 E^{\odot}_{cell} is:

- (1) x + 2y
 - (2) 2x + y (3) y x
- (4) y 2x
- 110. The standard reduction potentials of three metals A, B, and C are +0.5 V, -3.0 V, and -1.2 V, respectively. The order of reducing power of these metals is
 - (1) B > C > A
- (2) A > B > C
- (3) C > B > A
- (4) A > C > B
- 111. Calculate the maximum work that can be obtained from the decimolar Daniell cell at 25°C.

Given:
$$E^{\odot}_{(Z_n^{2+}|Z_n)} = -0.76 \text{ V}$$
 and $E^{\odot}_{(C_u^{2+}|C_u)} = 0.34 \text{ V}$

- (1) 193.0 kJ
- (2) 212.3 kJ
- (3) 81.06 kJ
- (4) 40.53 kJ
- 112. Stronger the oxidizing agent, greater is the
 - (1) Standard reduction potential
 - (2) Standard oxidation potential
 - (3) Ionic nature
 - (4) None
- 113. Consider the cell

$$Ag(s) \mid AgBr(s) Br^{\odot}(aq) \parallel AgCl(s), Cl^{\odot}(aq) \mid Ag(s)$$

at 298 K. The $K_{\rm sp}$ of AgBr and AgCl, respectively are 5×10^{-13} and 1×10^{-10} . At what ratio of [Br $^{\odot}$] and [Cl $^{\odot}$] ions, EMF_{cell} would be zero?

- (1) 200:1
- (2)1:200
- (3)1:100
- (4) 1:500

114. The pH of LHE in the following cell is:

 $Pt \mid H_2(1 \text{ atm}) \mid H^{\oplus}(x \text{ M}) \parallel H^{\oplus}(0.1 \text{ M}) \mid H_2(0.1 \text{ atm}) \mid Pt$ $E_{\rm cell} = 0.295 \text{ V}.$

- (1) 6.5
- (2) 6.0
- (3) 5.5
- (4) 4.0

115. At what concentration of [OH] does the following half reaction has a potential of 0 V when other species are at

$$NO_3^{\odot} + H_2O + 2e^- \longrightarrow NO_2^{\odot} + 2OH; E_{cell}^{\odot} = -0.06 \text{ V}$$

- (1) 2.0 M
- (2) 1.0 M
- (3) 0.1 M
- (4) 0.01 M

116. If hydrogen electrodes dipped in two solutions of pH = 3 and pH = 6 are connected by a salt bridge, the EMF_{cell} is

- (1) 0.052 V
- (2) 0.104 V
- (3) 0.177 V
- (4) 0.3 V

117. Consider the cell reaction:

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Mg^{2+}(aq)$$

If $E^{\ominus}_{Mg^{2+} \mid Mg(s)}$ and $E^{\ominus}_{Cu^{2+} \mid Cu(s)}$ are -2.37 and 0.34 V, respectively. E^{Θ}_{cell} is

- (1) 2.03 V
- (2) -2.03 V (3) -2.71 V (4) 2.71 V

118. E^{\odot}_{red} of different half cells are given as:

$$E^{\Theta}_{\text{Cu}^{2+}|\text{Cu}} = 0.34 \text{ V}, E^{\Theta}_{\text{Zn}^{2+}|\text{Zn}} = -0.76 \text{ V}.$$

$$E_{\text{Ag}}^{\oplus}|_{\text{Ag}} = 0.80 \text{ V}, E_{\text{Mg}}^{\ominus}|_{\text{Mg}}^{2+}|_{\text{Mg}} = -2.37 \text{ V}.$$

In which cell ΔG^{\odot} is most negative?

- (1) $Zn \mid Zn^{2+}(1 M) \parallel Mg^{2+}(1 M) \mid Mg$
- (2) $Zn \mid Zn^{2+}(1 M) \parallel Ag^{\oplus}(1 M) \mid Ag$
- (3) $Cu \mid Cu^{2+}(1 \text{ M}) \parallel Ag^{\oplus}(1 \text{ M}) \mid Ag$
- (4) $Ag \mid Ag^{\oplus}(1 M) \parallel Mg^{2+}(1 M) \mid Mg$

119. For the reaction:

$$A + 2B^{3+} \longrightarrow 2B^{2+} + A^{2+}$$

 E^{\odot} of the given redox reaction is:

$$A^{2+} + 2e^{-} \longrightarrow A$$
 $E^{\odot} = x V$

$$B^{3+} + e^- \longrightarrow B^{2+} \quad E^{\odot} = y V$$

(1)
$$y = 2y$$

(2) x + y/2 (3) x - y

(4) y - x

120. Excess of solid AgCl is added to a 0.1 M solution of Br[⊙] ions. E^{\odot} for half cell is:

$$AgBr + e^{-} \longrightarrow Ag + Br^{\ominus}; E^{\ominus} = 0.095 V$$

$$AgCl + e^{-} \longrightarrow Ag + Cl^{\odot}; E^{\odot} = 0.222 \text{ V}$$

The value of [Br[⊙]] ion at equilibrium is:

[Given: Antilog (2.152) = 142]

- (1) 0.0317 M
- (2) 0.013 M
- (3) 0.99 M
- (4) 0.099 M

Electrolysis

- 121. Which of the following solutions can be safely stored in a copper vessel?
 - (1) $ZnSO_{\Lambda}$
- $(2) AgNO_3$ $(3) AuCl_3$
- (4) All of them
- 122. By virtue of Faraday's second law of electrolysis, the electrochemical equivalent of the two metals liberated at the electrodes has the same ratio as that of their
 - (1) Atomic masses
- (2) Molecular masses
- (3) Equivalent masses
- (4) Any of three
- 123. 0.5 F of electricity is passed through 500 mL of copper sulphate solution. The amount of copper which can be deposited will be
 - (1) 63.5 g
- (2) 31.75 g
- (3) 15.8 g
- (4) Unpredictable
- 124. On carrying out the electrolysis of acidified water, the volume of hydrogen liberated at STP condition is 22.41 The volume of oxygen liberated is
 - (1) 22.4 L
- (2) 44.8 L
- (3) 11.2 L
- (4) 2.24 L
- 125. During the electrolysis of the aqueous solution of conner sulphate using Pt electrodes, the reaction taking place at anode electrode is
 - (1) $Cu^{2+} + 2e^{-} \longrightarrow Cu$
 - (2) $Cu \longrightarrow Cu^{2+} + 2e^{-}$
 - $(3) 2H_2O \longrightarrow 4H^{\oplus} + O_2 + 4e^{-}$
 - (4) $H_2O + e^- \longrightarrow \overset{\circ}{OH} + 1/2H_2$
- 126. In passing 3 F of electricity through three electrolytic cells connected in series containing Ag[⊕], Ca²⁺, and Al³⁺ ions. respectively. The molar ratio in which the three metal ions are liberated at the electrodes is
 - (1) 1 : 2 : 3
- (2) 2 : 3 : 1
- (3) 6:3:2
- (4) 3:4:2
- 127. During electrolysis of fused calcium hydride, the hydrogen is produced at
 - (1) Cathode
 - (2) Anode
 - (3) Hydrogen is not liberated at all
 - (4) H₂ produced reacts with oxygen to form water.
- 128. Which of the following is anodic reaction?
 - (1) $SO_4^{2-} + H_2O \longrightarrow H_2SO_4 + 1/2O_2 + 2e^-$
 - $(2) H^{\oplus} + e^{-} \longrightarrow 1/2H_2$
 - $(3) Ag^{\oplus} + e^{-} \longrightarrow Ag$
 - (4) None of these
- 129. The charge required for the reduction of 1 mol of $Cr_2O_1^{-2}$ ions to Cr³⁺ is
 - (1) 96500 C
- (2) $2 \times 96500 \, C$
- $(4) 6 \times 96500 C$
- 130. In order to completely oxidize 0.1 mol of MnO₄ is permanganate ion. The quantity of electricity required is
 - (1) 96500 C
- $(2) 2 \times 96500^{\circ}C$
- (3) 9650 C
- (4) 96.50 C

_	For the electrolytic production of NaClO ₄ from NaClO ₅ to the reaction NaClO ₆ + H.O. NaClO ₇ +	10,	(1) 1.59 g	(2) 3.18 g	(3) 6.35 g	(4) 12.70 g
	according to the reaction reactor $1130 \rightarrow 1800_4$	112.	Which of the	following is	a strong electr	olyte?
	How many faradays of electricity would be required	d to	(1) Ca(NO ₃) ₂		(2) HCN	
	produce 0.5 mole of NaClO ₄ ?		(3) H_2SO_3	2	(4) NH₄OH	
	(1) 1 (2) 2 (3) 3 (4) 1.5	142		e of 0.1 N FeS	4	dized by a current
132.	How many coulombs are required for the oxidation	n of 143.	of 2 ampere		, , , , , , , , , , , , , , , , , , , ,	
	1 mol of H_2O to O_2 ?		(1) 0.746 L		(2) 7.46 L	
	(1) 93000 C (2) 1.93×10^5 C		(3) 1.482 L		(4) 0.373 L	
	(3) $9.65 \times 10^4 \mathrm{C}$ (4) $19.3 \times 10^2 \mathrm{C}$, ,	M colution of		ectrolyzed with a
133.	On electrolysis of a solution of dilute H ₂ SO ₄ betw	reen 144.	500 mL of 1	mneres for 1	hour. What is	ectrolyzed with a the normality of
	platinum electrodes, the gas evolved at the anode is			g CuCl ₂ solut		•
	(1) SO_2 (2) SO_3 (3) O_2 (4) H_2			(2) 0.15		(4) 1.0
134.	In electrolysis of very dilute NaOH using platin	num 145 .	Ionic strength			
	electrodes	1450			(3) 0.9	(4) 0.8
	(1) H ₂ is evolved at cathode and O ₂ at anode (2) NH ₃ is produced at anode	146.	Ionic strength	` '		
	(3) Cl ₂ is obtained at cathode	140.		(2) 1.2		(4) 1.8
	(4) O ₂ is produced at cathode and H ₂ at anode	147	` /			ng equal volumes
125	During the electrolysis of fused NaCl, which reaction oc		-	Cl and 0.02 N		
135.	at anode?	cuis			(3) 0.0325	(4) 0.0216
	(1) Chloride ions are oxidized	148.				lytic oxidation of
	(2) Chloride ions are reduced		H ₂ SO ₄ as			
	(3) Sodium ions are oxidized		$2H_2SO_4 \longrightarrow$	$H_2S_2O_8 + 2H_2S_2O_8 + 2H_2$	$\mathbf{H}^{\oplus} + 2e^{-}$	
	(4)Sodium ions are reduced					such electrolysis
136.	Two platinum electrodes were immersed in a solu					uced at STP. The
	of CuSO ₄ and electric current was passed through		_	S ₂ O ₈ formed i		
	solution. After some time, it was found that colour of Cu	The	, ,		(3) 14.55 g	
	disappeared with evolution of gas at the electrode. colourless solution contains	149.		•	-	passing 0.1 A of
	(1) Platinum sulphate (2) Copper hydroxide		acetate	os s, inrough a	n aqueous soru	tion of potassium
	(3) Copper sulphate (4) Sulphuric acid			(2) 11 2 mL	(3) 89.6 mL	(4) 44 8 mI
137.	When electricity is passed through a solution of AlCl ₃	and 150.	The mass of			(1) 11.0 III.2
	13.5 g of Al is deposited, the number of Faraday must	be		(2) 0.6 g	(3) 6.0 g	(4) 60 g
	(1) 0.5 (2) 1.0 (3) 1.5 (4) 2.0	151				passing 0.2 A of
138.	What weight of copper will be deposited by pas	sing			-	lution of sodium
	2 faradays of electricity through a cupric salt (atomic we	eignt	fumarate is			
	of $Cu = 63.5$)? (1) 2.0 (2) 3.175 (3) 63.5 (4) 127.0		(1) 22.4 mL	(2) 11.2 mL	(3) 89.6 mL	(4) 44.8 mL
139	(1) 2.0 (2) 3.175 (3) 63.5 (4) 127.0 • A solution of 9.65 A flowing for 10 min deposits 3.0 g o	f the 152.				de on electrolysis
	metal which is monovalent. The atomic mass of the n	netal		odium succina		
	is (*) O/ 5				Cathode: H ₂	
146	(1) 10 (2) 50 (3) 30 (4) 96.5	How		-	Cathode: H ₂	
14()	 A certain current liberates 0.5 g of hydrogen in 2 hours. I many grams of copper can be liberated by the same current. 	rrent		Sthene $+$ H ₂ , (Sthyne $+$ H $=$ C		
	flowing for the same time in a copper sulphate solution	n? 153.	A current str	Ethyne + H ₂ , C ength of 1.0	A is passed for	or 96.5 s through
	(1) 12.7 g (2) 15.9 g (3) 31.8 g (4) 63.5 g		100 mL of a s	solution of 0.0	5 M KCl. The	concentration of
141	· The mass of copper that will be deposited at cathod	le in when			ect to OH ion:	

electrolysis of 0.2 M solution of copper sulphate when

a quantity of electricity equal to that required to liberate

2.24L of hydrogen from 0.1 M aqueous H_2SO_4 is passed

(atomic mass of Cu = 63.5) will be

(1) 0.005 M (2) 0.05 M (3) 0.01 M(4) 0.001 M 154. In Q.153, pH of the final solution will be (3) 11.7(4)3

(1) 12

(2) 2

	$2H_2O \longrightarrow 4H^{\oplus} + O_2 + 4e^-$	165. Chromium plating can involve the electrolysis of an acidified mixture of chromic			
	O ₂ formed at NTP due to passage of 2 amperes of current for 96 seconds is	chromium sulphate. If during electrolysis the article being			
	(1) 0.112 L (2) 0.224 L (3) 11.2 L (4) 22.4 L				
156.	. During electrolysis of acidified water, O_2 gas is formed at	tong heing discharged must be tassamme alome w.			
	the anode. To produce O ₂ gas at the anode at the rate of	$Cr = 52$ and 1 mole of gas at room temperature and n_{reso} .			
	0.224 mL per second at STP, current passed is	occupies a volume of 24 diff)			
	(1) 0.224 A (2) 2.24 A (3) 9.65 A (4) 3.86 A	(1) -1 (2) Zero (3) $+1$ (4) $+2$			
157	. The gas evolved at the anode when K_2SO_4 (aq) is electrolyzed between Pt electrodes is	166. Which of the following does not evolve oxyzen at anode when the electrolysis is carried out?			
	(1) O ₂ (2) H ₂ (3) SO_2 (4) SO_3	(1) Dilute H ₂ SO ₄ with Pt electrodes			
158	3. A quantity of electrical charge that brings about the	(2) Fused sodium hydroxide with Pt electrodes			
130	deposition of 4.5 g Al from Al ³⁺ at the cathode will also	(3) Acidic water with Pt electrodes(4) Dilute sulphuric acid using Cu electrodes			
	produce the following volume (STP) of H ₂ (g) from H [⊕] at				
	the cathode	167. A constant current was passed through a solution of AuCl. 9			
	(1) 44.8 L (2) 22.4 L (3) 11.2 L (4) 5.6 L	ion between gold electrodes. After a period of 10.0 min.			
159	. 100 mL of a buffer of 1 M NH ₃ (aq) and 1 M NH ₄ $^{\oplus}$ (aq) are	the increase in the weight of cathode was 1.314 g. The			
	placed in two voltaic cells separately. A current of 1.5 A is	total charge passed through solution is (atomic weight of			
	passed through both cells for 20 min. If the electrolysis of	AuCl ₄ $^{\circ}$ = 339) (1) 1.16 × 10 ⁻² F (2) 3.5 × 10 ⁻² F			
	water only takes place:	(3) $2 \times 10^{-2} \mathrm{F}$ (4) $4 \times 10^{-3} \mathrm{F}$			
	$2H_2O + O_2 + 4e^- \longrightarrow 4OH \text{ (RHS)}$	168. A current of 3 A was passed for 1 hour through an electrolyte			
	$2H_2O \longrightarrow H^{\oplus} + O_2 + 4e^-$ (LHS), then	solution of $A_x B_y$ in water. If 2.977 g of A (atomic weight			
	(1) pH of LHS half cell will increase.	106.4) was deposited at cathode and B was a monovalent			
	(2) pH of RHS half cell will increase.	ion, the formula of electrolyte was			
	(3) pH of both half cells will increase.	(1) AB_2 (2) AB (3) AB_3 (4) AB_4			
	(4) pH of both half cells will decrease.	169. Total charge required to convert three moles of Mn_3O_4 to			
160.	Which metal can deposit copper from copper sulphate	MnO ₄ ²⁻ in presence of alkaline medium			
	solution?	(1) 10 F (2) 20 F (3) 30 F (4) 40 F			
1.1	(1) Mercury (2) Iron (3) Gold (4) Platinum	170. A current of 965 A is passed for 1 s through 1L solution			
161.	On the basis of position in the electrochemical series, the	of 0.02 N NiSO ₄ using Ni electrodes. What is the new			
	metal which does not displace H_2 from water and acid is:	concentration of NiSO ₄ ?			
162	(1) Hg (2) Al (3) Pb (4) Ba	(1) 0.01 N (2) 0.01 M (3) 0.002 M (4) 0.02 M			
102.	A dilute aqueous solution of sodium fluoride is electrolyzed, the products at the anode and cathode are	171. Which one is wrong if electrolysis of CH ₃ COONa (aq) is made using Pt electrodes?			
	(1) O_2 , H_2 (2) F_2 , Na (3) O_2 , Na (4) F_2 , H_2	(1) pH of solution increases.			
163.	Copper can be deposited from acidified copper sulphate and	(2) Molar ratio of gases at anode and cathode is 3:1.			
	alkaline cuprous cyanide. If the same current is passed for a definite time:				
		(3) [CH ₃ COO [⊙]] in solution decreases.			
	(1) The amount of copper deposited from acidic copper sulphate will be higher.	(4) The molar ratio of gases at anode and cathode is 2:1.			
		172. Select the wrong statement.			
	(2) The amount of copper deposited from alkaline cuprous cyanide will be higher.	(1) The electrolysis of molten CaH ₂ liberates H ₂ at cathode			
	(3) The same amount of copper will be deposited	(2) During the discharge of lead storage battery, surprise acid is consumed			
164.	(4) None of these. Silver is removed electrolytically for the second se	(3) Sulphur acts as a polymerizing agent in the vulcanization of rubber.			
	solution of AgNO ₃ by a current of 0.1 A. How long will it take to remove half of the silver from the solution?	(4) Galvanization of iron denotes coating with Zn.			

(2) 100 s

(4) 9650 s

(1) 0.1 s

(3) 965 s

3.94 Physical Chemistry

155. Assume that during the electrolysis of AgNO₃, only H₂O is

electrolyzed and O2 is formed as

- 173. Select the correct statement.
 - (1) Faraday represents 96500 coulombs per second.
 - (2) Coulomb represents one ampere for 1/2 second.
 - (3) Coulomb represents 1/2 ampere for 1 second.
 - (4) Coulomb represents charge of one mole electron.
- 174. The strongest oxidizing agent among the following is
 - $(1) K_2 Cr_2 O_7 (2) MnO_2$
- $(3) \text{ KMnO}_4$ $(4) \text{ Cl}_2$
- 175. The weakest oxidizing agent among the following is
 - $(2) F_2$ $(1) O_2$
- $(3) \text{ KMnO}_4$ $(4) \text{ Cl}_2$
- 176. Chromium plating is applied by electrolysis to objects suspended in a dichromate solution, according to the

following (unbalanced) half reaction:

$$Cr_1, O_7^{-2}$$
 (aq) + e^- + H^{\oplus} (aq) \longrightarrow $Cr(s)$ + $H_2O(l)$

How many hours would it take to apply a chromium plating of thickness 2.0×10^{-2} mm to a car bumper of surface area 0.25 m² in an electrolysis cell carrying a current of 75.0 A? [Density of chromium is 7.19 g cm⁻³]

- (1) 2.2 h
- (2) 1.5 h
- (3) 3.0 h
- (4) 0.25 h
- 177. During the electrolysis of $AgNO_3$, the volume of O_2 formed at STP due to passage of 2 A of current for 965 s is

 - (1) 0.112 L (2) 0.224 L (3) 11.2 L
- (4) 22.4 L
- 178. The number of atoms of Ca that will be deposited from a solution of CaCl₂ by a current of 25 mA for 60 s will be
 - (1) 4.68×10^{18}
- (2) 4.68×10^{15}
- $(3) 4.68 \times 10^{10}$
- (4) 2.34×10^{15}
- 179. During the electrolysis of aqueous solution of HCOOK, the number of gases obtained at cathode, anode, and total number of gases are
 - (1) 1, 2, 3
- (2) 1, 2, 2
- (3) 2, 1, 3
- (4) 2, 1, 2
- 180. During the electrolysis of acidified water, O_2 gas is formed at the anode. To produce O_2 gas at the anode at the rate of 0.224 mL per second at STP, the current passed is

 - (1) 0.224 A (2) 2.24 A
- (3) 9.64 A
- (4) 3.86 A
- 181. Number of electrons lost during electrolysis of $0.355~\mathrm{g}$ of Cl^{Θ} is $(N_A = Avogadro's number)$
- (1) 0.01 (2) $0.01N_A$ (3) $0.02N_A$
- 182. How many faradays are required to reduce one mole of MnO_4^{\ominus} to Mn^{2+} ?
 - (1) 1
- (2)5
- (3) 3
- (4) 2
- 183. Copper containing zinc as impurity is refined by electrolysis. The cathode and anode used are

Cathode

Anode

- (1) Pure copper
- Pure zinc
- (2) Pure zinc
- Pure copper
- (3) Pure copper
- Impure copper
- (4) Pure zinc
- Impure zinc
- 184. Which of the following reactions is/are possible at the anode?

- $(1) F_2 + 2e^- \longrightarrow 2F^{\odot}$
- (2) $2H^{\oplus} + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$
- (3) $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{-}$
- (4) $Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$
- 185. The number of moles of Zn2+ ions deposited when a current of 1.5 A is passed for 4 hours through a molten solution of a zinc salt. (Assume current efficiency to be 90%)
 - (1) 6.35
- (2) 0.1
- (3)0.4
- (4) None of these
- 186. Molten NaCl is electrolyzed in a cell called
 - (1) Downs cell
- (2) Castner cell
- (3) Kellner cell
- (4) Hall cell
- 187. A dilute aqueous solution of potassium fluoride is electrolyzed. The products at the anode and cathode are
 - (1) O₂ and K
- (2) O_2 and F_2
- (3) H₂ and F₂
- (4) O_2 and H_2
- 188. If 0.224 L of H₂(g) is formed at the cathode of one cell at STP, how much of Mg is formed at the cathode of the other electrolytic cell arranged in series?
 - (1) 0.24 g
- (2) 2.4 g
- (3) 0.48 g
- 189. A certain amount of charge is passed through acidified $\rm H_2O$. A total of 168 mL of $H_2(g)$ and $O_2(g)$ were evolved at STP. What is the magnitude of charge passed during electrolysis?
 - (1) 1930 C (2) 965 C
- (3) 482.5 C (4) 241.2 C
- 190. 1 L of 1 M CuSO₄ solution is electrolyzed using Pt cathode and Cu anode. After passing 2 F of electricity, the $[Cu^{2+}]$ will be
 - (1)0
- (2) M
- (3) M/2
- (4) M/4
- 191. How many Faradays are required to reduce 1 mole of BrO₃[©] to Br[⊙]?
 - (1)6
- (2)5
- (3)4
- (4)3
- 192. Which of the following aqueous solutions remains neutral after electrolysis?
 - $(1) K_2 SO_4$
- (2) NaCl
- (3) AgNO₃ (4) CuSO₄
- 193. Same quantity of current is passed through molten NaCl and molten cryolite containing Al₂O₃. If 4.6 g of Na was liberated in one cell, the mass of Al liberated in the other cell is
 - (1) 0.9 g
- (2) 1.8 g
- (3) 2.7 g
- (4) 3.6 g
- 194. Two platinum electrodes were immersed in a solution of $\mathrm{CuSO_4}$ and electric current was passed through the solution. After some time, it was found that the colour of CuSO₄ disappeared with the evolution of $O_2(g)$ at the electrode. Which statement is true regarding the resultant solution
 - having pH = X?
 - (1) $[Cu^{2+}] > [SO_4^{2-}]$ (2) $[Cu^{\oplus}] > [Cu^{2+}]$
 - (3) $[OH] > [H^{\oplus}]$
- (4) 7 > X

 3.96 Physical Chemistry 195. Molten Al₂O₃ is electrolyzed at 1000°C to furnish Al metal (atomic weight = 27 amu). How much electricity is required to prepare 5.12 kg of Al? 	III In general, with increase in concentration, the se
(1) 5.49×10^{10} C (2) 1.83×10^{7} C (3) 5.49×10^{4} C (4) 5.49×10^{7} C Conductance, specific, equivalent and Molar Conductance	then decreases with further increase in concentration (1) I, II, and III (2) I and II
196. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl, and KCl is (1) LiCl > NaCl > KCl (2) KCl > NaCl > LiCl	
(3) NaCl > KCl > LiCl (4) LiCl > KCl > NaCl The ion which has the lowest ionic mobility is	(1) $\frac{1000x}{N}$ (2) $\frac{1000}{Nx}$ (3) $\frac{1000N}{x}$ (4) $\frac{Nx}{1000}$

(4) Rb[⊕]

(4) 0.05

(4) 2.3

(4) 101.15

(2) Na^{\oplus} (3) K^{\oplus}

dissociation (α) of acetic acid?

(2) 0.48

(2)9.2

BaCl₂ at infinite dilution will be

(2) 203.0

(1) $\Lambda_{(MA)}^{\circ} = \Lambda_{(MCI)}^{\circ} + \Lambda_{(NaA)}^{\circ} + \Lambda_{(NaCI)}^{\circ}$

(2) $\Lambda^{\circ}_{(MA)} = \Lambda^{\circ}_{(MCI)} + \Lambda^{\circ}_{(NaA)} - \Lambda^{\circ}_{(NaCI)}$

(4) $\Lambda^{\circ}_{(MA)} = \Lambda_{(MCI)} + \Lambda_{(NaA)} - \Lambda_{(NaCI)}$

(3) $\Lambda^{\circ}_{(MA)} = \lambda^{\circ}_{(M\bigoplus)} + \lambda^{\circ}_{(A\bigoplus)}$

 x_3 , respectively. $\Lambda^{\circ}_{\text{eq (BaSO}_a)}$ is

 x_3 , respectively. $\Lambda_{m(BaSO_4)}^{\circ}$ is:

 $(3) x_1 + x_2 - 2x_3$

 $(1) x_1 + x_2 - x_3$

(3) $x_1 + x_2 - 2x_3$

 $(1) x_1 + x_2 - x_3$

198. For a 0.01 M CH₃COOH solution, $\Lambda_{\rm m} = 7.8~\Omega^{-1}~{\rm cm^2~mol^{-1}}$

199. The resistance of a 0.1 N solution of acetic acid is 250Ω

200. The equivalent conductances of Ba²⁺ and Cl[⊙] are 63.5 ohm⁻¹

201. The equivalent conductance of any electrolyte MA at

202. Which of the following ions has the highest ionic mobility?

(1) Na^{\oplus} (2) F^{\ominus} (3) SO_{a}^{2-} (4) $\overset{\circ}{O}H$

203. Λ_{eq}° of BaCl₂, H₂SO₄, and HCl(aq) solutions are x_1, x_2 , and

204. Λ°_{m} of BaCl₂, H₂SO₄, and HCl(aq) solutions are x_1, x_2 , and

I. van't Hoff factor for 10⁻³ M CH₃COOH is 39/35

 $(\Lambda_{m}^{\circ} = 350 \text{ S cm}^{2} \text{ mol}^{-1} \text{ and } \kappa = 4 \times 10^{-5} \text{ S cm}^{-1}).$

205. Which of the following statements is/are correct?

(2) $x_1 - x_2 - x_3$

(2) $x_1 - x_2 - x_3$

 $(4) x_1 - 2x_2 + x_3$

 $(4) x_1 - 2x_2 + x_3$

infinite dilution $\Lambda^{\circ}_{(MA)}$ is (more than one correct answer)

cm² eq⁻¹ and 76 ohm⁻¹ cm² eq⁻¹, respectively, at infinite

dilution. The equivalent conductance (in ohm-1 cm2) of

if $\Lambda_{m}^{\circ} = 390 \ \Omega^{-1} \ cm^{2} \ mol^{-1}$. What is the degree of

when measured in a cell of cell constant 1.15 cm⁻¹. The

equivalent conductance (in ohm-1 cm2 eq-1) of 0.1 N acetic

(3) 0.02

(3) 18.4

(3)279.0

(1) Li[⊕]

(1) 0.20

acid is

(1)46.0

(1) 139.5

207. The units of conductivity of the solution are

conductivity of an electrolyte A₂B is

208. According to Kohlrausch law, the limiting value of molar

 $(1) \lambda_{(A\oplus)}^{\infty} + \lambda_{(B\ominus)}^{\infty} \qquad (2) \lambda_{(A\oplus)}^{\infty} - \lambda_{(B\ominus)}^{\infty}$

(3) $2\lambda_{(A^{\oplus})}^{\infty} + \frac{1}{2}\lambda_{(B^{\ominus})}^{\infty}$ (4) $2\lambda_{(A^{\oplus})}^{\infty} + \lambda_{(B^{\ominus})}^{\infty}$

209. The values of Λ_{eq}^{∞} for NH₄C1, NaOH, and NaCl are.

(4) It cannot be calculated from the data given

(1) Increase in the self ionization of water

(3) Decrease in the self ionization of water

(4) Decrease in the interionic forces

444.0 Ω^{-1} cm² mol⁻¹, respectively.

210. The increase in the molar conductivity of HCl with dilution

211. Calculate the solubility product of Co₂[Fe(CN)₆] in water

Given, conductivity of saturated solutions of Co₂[Fe(CN)]

is $2.06 \times 10^{-6} \ \Omega^{-1} \ cm^{-1}$ and that of water used is

 $4.1 \times 10^{-7} \ \Omega^{-1} \ \text{cm}^{-1}$. The ionic molar conductivities of

 Co^{2+} and $[\text{Fe}(\text{CN})_6]^{4-}$ are 86.0 Ω cm² mol⁻¹ and

212. The dissociation of a weak electrolyte obeys the law of mass

213. The increase in the value of molar conductivity of acetic

(1) Decrease in interionic forces and increases in α .

(2) 7.87×10^{-6}

(4) 7.87×10^{-9}

(2) Arrhenius

(4) None of these

respectively, 149.74, 248.1, and 126.4 ohm⁻¹ cm² eq⁻¹. The

(2) ohms

(4) ohm⁻¹ eq⁻¹

 $(1) \text{ ohm}^{-1}$

(3) $ohm^{-1} cm^{-1}$

value of Λ_{eq}^{∞} NH₄OH is

(2) Hydrolysis of HCl

(1) 371.44

(2) 271.44

(3)71.44

at 25°C.

(1) 7.87×10^{-17}

(3) 7.87×10^{-18}

(1) Ostwald

(3) Berzelius

action. It was found by

acid with dilution is due to

- (2) Increase in the degree of ionization and interionic forces.
- (3) Increase in self ionization of water.
- (4) None of these
- The value of molar conductivity of HCl is greater than that of NaCl at a particular temperature because
 - (1) Molecular mass of HCl is less than that of NaCl
 - (2) Velocity of H[⊕] ions is more than that of Na[⊕] ions.
 - (3) HCl is strongly acidic
 - (4) Ionization of HCl is larger than that of NaCl
- 215. 10800 C of electricity passed through the electrolyte deposited 2.977 g of metal with atomic mass 106.4 g mol⁻¹. The charge on the metal cation is
 - (1) + 4
- (2) +3
- (4) + 1
- 216. The two Pt electrodes fitted in a conductance cell are 1.5 cm apart while the cross-sectional area of each electrode is 0.75 cm. What is the cell constant?
 - (1) 1.125
- (2) 0.5 cm
- (3) 2.0 cm^{-1} (4) 0.2 cm^{-1}
- 217. For an electrolyte solution of $0.05 \text{ mol } L^{-1}$, the conductivity has been found to be 0.0110 S cm⁻¹. The molar conductivity
 - (1) $0.055 \text{ S cm}^2 \text{ mol}^{-1}$
- (2) 550 S cm² mol⁻¹
- (3) $0.22 \text{ S cm}^2 \text{ mol}^{-1}$
- (4) 220 S cm² mol⁻¹
- 218. If the specific conductance of 1 M H₂SO₄ solution is 26×10^2 S cm² mol⁻¹, then the equivalent conductivity would be
 - (1) $1.3 \times 10^2 \,\mathrm{S} \,\mathrm{cm}^{-1}$
- (2) $1.6 \times 10^2 \,\mathrm{S} \,\mathrm{cm}^{-2}$
- (3) 13 S cm² mol⁻¹
- (4) $1.3 \times 10^3 \text{ S cm}^2 \text{ mol}^{-1}$
- 219. The highest electrical conductivity of the following aqueous solutions is of
 - (1) 0.1 M acetic acid
 - (2) 0.1 M chloro acetic acid
 - (3) 0.1 M fluoro acetic acid
 - (4) 0.1 M difluoro acetic acid
- 220. Which of the following statements is wrong?
 - (1) The conductance of 1 cm³ of a material is called specific conductance.
 - (2) Specific conductance increases while equivalent conductance decreases on progressive dilution.
 - (3) The limiting equivalent conductances of weak electrolytes cannot be determined by the extrapolation of the plot of Λ against concentration.
 - (4) The conductivity of metals is due to the movement of electrons.
- 221. Which of the following statements is correct?
 - (1) Specific conductance of a solution decreases with dilution, whereas molar conductance increases with
 - (2) Specific conductance of a solution increases with dilution, whereas molar conductance decreases with dilution.

- (3) Both specific conductance and molar conductance decrease with dilution.
- (4) Both specific conductance and molar conductance increase with dilution.
- 222. For a dilute solution of a strong electrolyte, the variation of molar conductivity with concentration is given by
 - (1) $\Lambda_{\rm m} = \Lambda_{\rm m}^{\circ} + Ac$ (2) $\Lambda_{\rm m} = \Lambda_{\rm m}^{\circ} Ac$

 - (3) $\Lambda_{\rm m} = \Lambda_{\rm m}^{\circ} + A\sqrt{c}$ (4) $\Lambda_{\rm m} = \Lambda_{\rm m}^{\circ} A\sqrt{c}$
- 223. A cell constant is generally found by measuring the conductivity of aqueous solution of
 - (1) BaCl₂
- (2) KCl
- (3) NaCl
- (4) MgCl₂
- 224. A solution of sodium sulphate was electrolyzed using some inert electrode. The products at the electrodes are
 - $(1) O_2, H_2$

- (2) O_2 , Na (3) O_2 , SO_2 (4) O_2 , $S_2O_8^{2-}$
- 225. The resistance of 1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant 1.15 cm⁻¹. The equivalent conductance (in ohm-1 cm2 eq-1) of 1 N acetic acid is
 - (1)4.6
- (2)9.2
- (3) 18.4
- (4) 0.023
- 226. Given the ionic equivalent conductivities for the following ions:

$$\lambda^{\circ}_{eq} K^{\oplus} = 73.5 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq}^{-1}$$
 $\lambda^{\circ}_{eq} \text{ Al}^{3+} = 149 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq}^{-1}$
 $\lambda^{\circ}_{eq} \text{ SO}_4^{2-} = 85.8 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq}^{-1}$

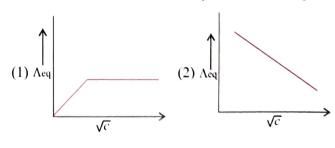
The $\Lambda_{\rm eq}^{\circ}$ for potash alum (K_2SO_4·Al_2(SO_4)_3·24H_2O) is:

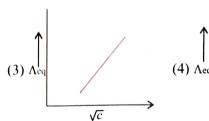
- (1) 215.92
- (2)348.3
- (3) 368.2
- **227.** Given the ionic conductance of $\stackrel{COO^{\ominus}}{|}_{COO^{\ominus}}$, K^{\oplus} , and Na^{\oplus} are

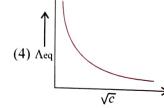
74, 50, and 73 cm² ohm⁻¹ eq⁻¹, respectively. The equivalent

conductance at infinite dilution of the salt

- (1) $197 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq}^{-1}$ (2) $172 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq}^{-1}$
- (3) $135.5 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq}^{-1}$ (4) $160.5 \text{ cm}^2 \text{ ohm}^{-1} \text{ eq}^{-1}$
- 228. The variation of equivalent conductance of strong electrolyte with $\sqrt{\text{concentration}}$ is correctly shown in the figure





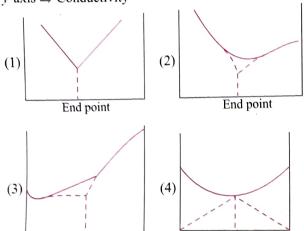


229. The electrical conductivity of a solution serves as a means of determining the end point in a chemical reaction, involved in the titration of acids, bases, or precipitation. Which of the following conductometric titrations represent the curve of HCl vs NH₄OH

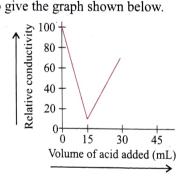
x-axis \Rightarrow Volume of alkali added

End point

v-axis \Rightarrow Conductivity



230. 20 mL of KOH solution was titrated with 0.20 M H₂SO₄ solution in a conductivity cell. The data obtained were plotted to give the graph shown below.



The concentration of the KOH solution was

- (1) $0.30 \text{ mol } L^{-1}$
- $(2) 0.15 \text{ mol } L^{-1}$

End point

- (3) $0.12 \text{ mol } L^{-1}$
- (4) $0.075 \text{ mol } L^{-1}$
- 231. $\kappa = 4.95 \times 10^{-5} \, \mathrm{S \ cm^{-1}}$ for a 0.001 M solution. The reciprocal of the degree of dissociation of acetic acid, if $\Lambda_{m}^{\ \ \circ}$ for acetic acid is 400 S cm⁻² mol⁻¹ is:
 - (1)7
- (2) 8
- (4) 10
- **232.** What is the value of pK_b (CH₃COO $^{\odot}$) if

 $\Lambda_{m}^{\circ} = 390 \text{ S cm}^{-1} \text{ mol}^{-1} \text{ and } \Lambda_{m} = 7.8 \text{ S cm}^{2} \text{ mol}^{-1} \text{ for } 0.04 \text{ M}$ of CH₃COOH at 25°C?

- (1)9.3
- (2)9.2
- (3)4.7
- (4)4.8
- 233. In Hall's process, in the production of Al, carbon is used as the anode material. The reactions are
 - (1) Anode: $A1^{3+} + 3e^{-} \longrightarrow A1$

Cathode: $C(s) + 2O^{2-} \longrightarrow CO_2(s) + 4e^{-s}$

(2) Anode: $C(s) + 2O^{2-} \longrightarrow CO_2(g) + 4e^{-}$

Cathode: Al³⁺ + 3 $e^- \longrightarrow$ Al

(3) Anode: A1 \longrightarrow Ae³⁺ + e^-

Cathode: $CO_2 + 4e^- \longrightarrow C(s) + 2O^{2-}$

(4) None of these

- 234. CH₃COOH is titrated with NaOH solution. Which of the following statements is true?
 - (1) Conductance decreases upto equivalence point, after which it increases.
 - (2) Conductance increases upto equivalence point, after which it decreases.
 - (3) Conductance first decreases (but not rapidly) and then increases upto equivalence point and then increases rapidly after equivalence point.
 - (4) None of these.

Commercial Cells and Corrosion

- 235. In a Ni-Cd battery
 - (1) All the reactants and products in the overall reaction are in the liquid state.
 - (2) The voltage of the cell changes rapidly.
 - (3) The electrolyte used is an alkali solution.
 - (4) All of the above are true.
- 236. Rusting of iron is
 - (1) A decomposition process
 - (2) A photochemical process
 - (3) An electrochemical
 - (4) A reduction process
- 237. The cell reaction of a fuel cell is
 - $(1) 2H_2O(1) \longrightarrow 2H_2(g) + O_2(g)$
 - $(2) 2H₂(g) + O₂(g) \longrightarrow 2H₂O(1)$
 - (3) $CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$
 - $(4) C(s) + O_2(g) \longrightarrow CO_2(g)$
- 238. The cathode reaction during the charging of a lead-acid battery leads to the
 - (1) Formation of PbSO₄
 - (2) Reduction of Pb²⁺ to Pb
 - (3) Formation of PbO₂
 - (4) Deposition of Pb at the anode
- 239. Which of the following cells is rechargeable?
 - (1) Lead storage cell
 - (2) Ni-Cd cell
 - (3) Edison cell (Iron-nickel cell)
 - (4) All of these
- 240. In a lead storage battery
 - (1) Pb is oxidized to PbSO₄ at the anode
 - (2) PbO₂ is reduced to PbSO₄ at the cathode
 - (3) Both electrodes are immersed in the same aqueous solution of H₂SO₄
 - (4) All of the above are true
- 241. In the rusting of iron, which of the following cell reactions occurs at the cathode?
 - (1) Fe^{2+} | Fe
- (2) $O_2 \mid H_2O$
- (3) Fe^{3+} | Fe^{2+}
- (4) Fe | Fe^{3+}

Which of the following reactions occurs at the anode during the recharging of lead storage battery?

 $(1) Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^{-1}$

(2) Pb + PbO₂ + H₂SO₄ \longrightarrow 2PbSO₄ + 2H₂O

 $(3) \text{ PbSO}_4 + 2e^- \longrightarrow \text{Pb} + \text{SO}_4^{2-}$

 $(4) \text{ PbSO}_4 + 2\text{H}_2\text{O} \longrightarrow \text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 + 2e^{-1}$

13. In H₂-O₂ fuel cell, the reaction occurring at cathode is (1) $2H_2 + O_2 \longrightarrow 2H_2O(1)$

 $(2) H^{\oplus} + OH \longrightarrow H_2O$

 $(3) O_2 + 2H_2O + 4e^- \longrightarrow 4 OH$

 $(4) H^{\oplus} + e^{-} \longrightarrow \frac{1}{2} H_2$

244. In which of the following will the corrosion of iron be most rapid?

(1) In pure water

(2) In pure oxygen

(3) In air and moisture

(4) In air and saline water

145. Rust is a mixture of

(1) FeO and Fe(OH),

(2) FeO and Fe(OH)₃

(3) Fe_2O_3 and $Fe(OH)_3$

(4) Fe_3O_4 and $Fe(OH)_3$

246. Galvanized iron sheets are coated with

(1) Copper (2) Nickel

(3) Zinc

(4) Carbon

247. An example of a simple fuel cell is

(1) Lead storage battery

(2) Leclanche cell

(3) H₂-O₂ cell

(4) All of these

248. The rusting of iron takes place as follows

$$2H^{\oplus} + 2e^{-} + \frac{1}{2}O_{2} \longrightarrow H_{2}O(1); E^{\ominus} = +1.23 \text{ V}$$

$$Fe^{2+} + 2e^{-} \longrightarrow Fe(s); E^{\odot} = -0.44 \text{ V}$$

 ΔG^{\ominus} for the net process is

(1) -322 kJ mol⁻¹

 $(2) -161 \text{ kJ mol}^{-1}$

 $(3) -152 \text{ kJ mol}^{-1}$

 $(4) - 76 \text{ kJ mol}^{-1}$

²⁴⁹. The combustion of butane in O_2 at 1 bar and 298 K shows a decrease in free energy equal to $2.75\times 10^3~kJ~mol^{-1}$ in a fuel cell. K and E^{\odot} of the fuel cell are

(1) 9.55×10^{482} , 1.096 V (2) 9.55, 1.096 V

(3) 1.023×10^{966} , 2.85 V (4) 5.5×10^{484} , 0.55 V

250. The EMF of Ni-Cd battery is dependent of:

 $(1) Cd(OH)_2$

(2) Ni(OH)₂

(3) OH

(4) None of these

251. The rusting of iron takes place as follows:

 $2H^{\oplus} + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(1);$

 $E^{\odot} = \pm 1.23 \text{ V}$

 Fe^{2+} (aq) + $2e^- \longrightarrow Fe(s)$;

 $E^{\odot} = -0.44 \text{ V}$

Calculate ΔG^{\odot} for the net process.

(1) -322 kJ mol⁻¹

 $(2) -152 \text{ kJ mol}^{-1}$

 $(3) - 76 \text{ kJ mol}^{-1}$

 $(4) -161 \text{ kJ mol}^{-1}$

Miscellaneous

252. Which of the following aqueous solution produces metal after electrolysis?

(1) $K_2Cr_2O_7$

(2) KMnO₄

(3) CH₃COONa

(4) CuCl₂

253. Ammonium perchlorate, NH₄ClO₄, used in the solid fuel in the booster rockets on the space shuttle, is prepared from sodium perchlorate, NaClO₄, which is produced commercially by the electrolysis of a hot, stirred solution of sodium chloride. How many faradays are requred produce 1.0 kg of sodium perchlorate?

 $NaCl + 4H_2O \longrightarrow NaClO_4 + 4H_2$

(1) 40.3

(2) 18.3

(3) 31.6

(4) 65.3

254. When a lead storage battry is charged it acts as:

(1) A fuel cell

(2) An electrolytic cell

(3) A galvanic cell

(4) A concentration cell

255. Equivalent conductivity of Fe₂(SO₄)₃ is related to molar conductivity by the expression:

(1) $\Lambda_{eq} = \Lambda_{m}$

(2) $\Lambda_{\rm eq} = \Lambda_{\rm m}/3$

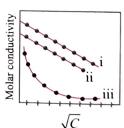
(1) $\Lambda_{eq} = \Lambda_{m}$ (2) $\Lambda_{eq} = \Lambda_{m}/3$ (3) $\Lambda_{eq} = 3\Lambda_{m}$ (4) $\Lambda_{eq} = \Lambda_{m}/6$

256. The specific conductance of a saturated solution of silver bromide is κ Scm⁻¹. The limiting ionic condictivity of Ag[⊕] and Br^{Θ} ions are x and y, respectiely. The solubility of silver bromide in gL^{-1} is: (molar mass of AgBr = 188)

(2) $\frac{\kappa}{x+v} \times 188$

(3) $\frac{\kappa \times 1000 \times 188}{x + y}$ (4) $\frac{x + y}{\kappa} \times \frac{1000}{188}$

257. A graph was plotted between molar conductivity of various electrolytes (NaCl, HCl and NH₄OH) and \sqrt{C} (in mol L⁻¹). Correct set is:



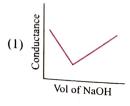
(1) I(NaCl), II(HCl), III(NH₄OH)

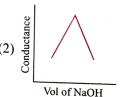
(2) I(HCl), II(NaCl), III(NH₄OH)

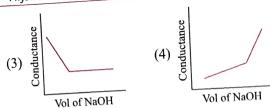
(3) I(NH₄OH), II(NaCl), III(HCl)

(4) I(NH₄OH), II(HCl), III(NaCl

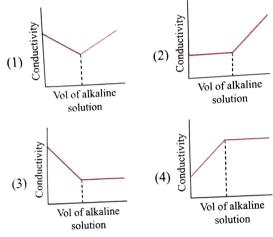
258. HNO₃(aq) is titrated with NaOH(aq) conductometrically, graphical representation of the titration is:



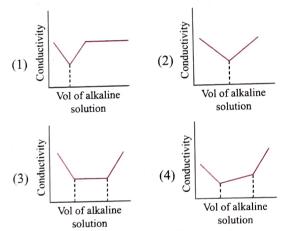




259. Which of the following plots will be obtained for a conductometric titration of strong acid against a weak base?



260. Conductometric titration curve of a equimolar mixture of a HCl and HCN with NaOH(aq) is:



261. A layer of chromium metal 0.25 mm thick is to be plated on an auto bumper with a total area of 0.32 m² from a solution containing CrO₄²⁻? What current flow is required for this electroplating if the bumper is to be plated in 60 s? The density of chromium metal is 7.20 g/cm³.

(1)
$$4.9 \times 10^3 \,\text{A}$$

(2)
$$1.78 \times 10^3 \,\mathrm{A}$$

(3)
$$5.3 \times 10^4 \,\mathrm{A}$$

(4)
$$10.69 \times 10^4 \,\mathrm{A}$$

262. Calculate the potential of a half cell having reaction:

$$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}(aq)$$
 in a solution buffered at pH = 3 and which is also saturated with 0.1 M H₂S(aq):

[Given:
$$K_{sp}$$
 (Ag₂S) = 10^{-49} , $K_{a_1} \cdot K_{a_2} = 10^{-21}$]
(1) 1.18 (2) 0.19

$$(3) -0.19 \text{ V}$$

263. Equivalent conductivity of BaCl₂, H₂SO₄ and HCl, are
$$x_1$$
, x_2 and x_3 Scm⁻¹ eq⁻¹ at infinite dilution. If conductivity of saturated BaSO₄ solution is x Scm⁻¹, then K_{sp} of BaSO₄ is:

$$(1) \ \frac{500x}{(x_1 + x_2 - 2x_3)}$$

(1)
$$\frac{500x}{(x_1 + x_2 - 2x_3)}$$
 (2) $\frac{10^6 x^2}{(x_1 + x_2 - 2x_3)^3}$

(3)
$$\frac{2.5 \times 10^5 x^2}{(x_1 + x_2 - x_3)^2}$$
 (4)
$$\frac{0.25 x^2}{(x_1 + x_2 - x_3)^2}$$

4)
$$\frac{0.25x^2}{(x_1 + x_2 - x_3)^2}$$

$$(x_1 + x_2 - x_3)$$
264. $Zn(s) \mid Zn(CN)_4^{2-}(0.5M), CN^{\Theta}(0.01) \parallel Cu(NH_3)_4^{2+}$

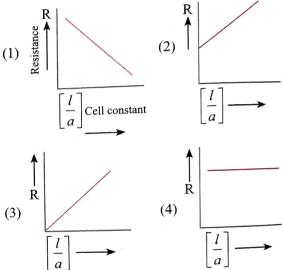
$$(0.5M), NH_3(1M) \mid Cu(s)$$

Given:
$$K_f$$
 of $Zn(CN)_4^{2-} = 10^{16}$, K_f of $Cu(NH_3)_4^{2+} = 10^{12}$

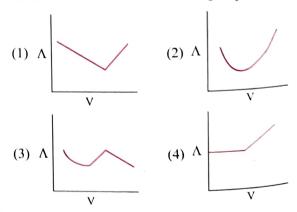
$$E_{\text{Zn}|\text{Zn}^{+2}}^{\circ} = 0.76 \text{ V} ; E_{\text{Cu}^{+2}|\text{Cu}}^{\circ} = 0.34 \text{ V}, \frac{2.303RT}{F} = 0.06$$

The emf of above cell is:

- (1) 1.22 V
- (2) 1.10 V
- (3) 0.98 V
- (4) None of these
- 265. Variation of resistance with increase in cell constant gives graph of the type



266. AgNO₃(aq) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plots of conductance Λ vs volume of AgNO₃(aq) is:

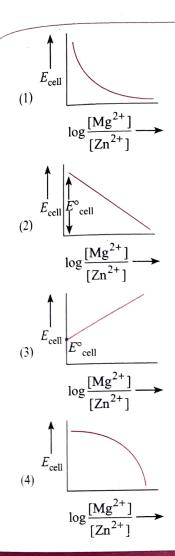


 $Mg(s)|Mg^{2+}(aq)||Zn^{2+}(aq)||Zn(s);$

$$E^{\circ} = +3.13^{\circ}$$

The correct plot of Ecell versus log represented as:

$$g \frac{[Mg^{2+}]}{[Zn^{2+}]} will^{bt}$$



Multiple Correct Answers Type

Electrochemical Cell

1. Consider the following concentration cell:

 $Zn(s) \mid Zn^{2+} \ (0.024 \ M) \parallel Zn^{2+} \ (0.480 \ M) \mid Zn(s)$

which of the following statements is/are correct?

(1) The EMF of the cell at 25° C is nearly +0.039 V.

(2) The EMF of the cell at 25° C is nearly -0.039~V.

(3) If water is added in LHE, so that the $[Zn^{2+}]$ is reduced to 0.012 M, the cell voltage increases.

(4) If water is added in LHE, so that the $[Zn^{2+}]$ is reduced to 0.012 M, the cell voltage decreases.

2. Given:

Oxidation: $H_2O_2 \longrightarrow O_2 + 2H^{\oplus} + 2e^ E^{\ominus} = -0.69 \text{ V};$ $E^{\odot} = -2.87 \text{ V};$

 $2F^{\ominus} \longrightarrow F_2 + 2e^-$

Reduction: $H_2O_2 + 2H^{\oplus} + 2e^- \longrightarrow 2H_2O \quad E^{\ominus} = 1.77 \text{ V};$ $E^{\odot} = -0.54 \text{ V};$ $2I^{\odot} \longrightarrow I_2 + 2e^-$

Which of the following statements is/are correct?

(1) H_2O_2 behaves as an oxidant for I^{\odot} .

(2) H_2O_2 behaves as a reductant for I_2 .

(3) H_2O_2 behaves as an oxidant for F^{\ominus} .

(4) H_2O_2 behaves as a reductant for F_2 .

3. Predict which of the following reactions would proceed spontaneously at 298 K?

(1) $Co(s) + Fe^{2+}(aq) \longrightarrow Co^{2+}(aq) + Fe(s)$

$$E^{\odot}_{\text{Co}^{2+}/\text{Co}} = -0.28 \text{ V}$$

 $E_{Co^{2+}/Co}^{\odot} = -0.28 \text{ V}$ (2) $Cd^{2+}(aq) + Fe(s) \longrightarrow Cd(s) + Fe^{2+}(aq)$

$$E^{\odot}_{\text{Cd}^{2+}/\text{Cd}} = -0.4 \text{ V}$$

 $(3) \operatorname{Cd}(s) + \operatorname{Co}^{2+}(\operatorname{aq}) \longrightarrow \operatorname{Cd}^{2+}(\operatorname{aq}) + \operatorname{Co}(s)$

$$E^{\odot}_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

(4) $Zn^{2+}(aq) + H_2 \longrightarrow Zn(s) + 2H^{\oplus}$ $E_{Fe^{2+}/Fe} = -0.44 \text{ V}$

$$E^{\odot}_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

4. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y[©] and 1 M Z[©] at 25°C. If the reduction potential is Z > Y > X, then

(1) Y will oxidize X only

(2) Y will oxidize Z only

(3) Z will oxidize X and Y

(4) Z will reduce both X and Y

5. Which of the following changes will increase the EMF of the cell

 $Co(s) \mid CoCl_2(M_1) \parallel HCl(M_2) \parallel (H_2, g)$ Pt?

(1) Increase the volume of CoCl₂ solution from 100 mL to

(2) Increase M_2 from 0.01 M to 0.50 M.

(3) Increase the pressure of the $H_2(g)$ from 1.0 to 2.0 atm.

(4) Increase M_1 from 0.01 M to 0.50 M.

6. Given:

$$E_{\text{Ag} \oplus | \text{Ag}}^{\ominus} = 0.80 \text{ V}, E_{\text{Mg}^{2+}| \text{Mg}}^{\ominus} = -2.37 \text{ V};$$

 $E_{\text{Cu}^{2+}| \text{Cu}}^{\ominus} = 0.34 \text{ V}, E_{\text{Hg}^{2+}| \text{Hg}}^{\ominus} = 0.79 \text{ V}$

Which of the following statements is/are incorrect?

(1) AgNO₃ can be stored in copper vessel.

(2) Cu(NO₃)₂ can be stored in magnesium vessel.

(3) CuCl₂ can be stored in silver vessel.

(4) HgCl₂ can be stored in copper vessel.

7. 100 mL of buffer of 1 M NH₃(aq) and 1 M NH₄[⊕](aq) are placed in two compartments of a voltaic cell separately. A current of 1.5 A is passed through both cells for 20 min. If only electrolysis of water takes place, then

(1) pH of LHE half cell will increase

(2) pH of RHE half cell will increase

(3) pH of both half cell will increase

(4) pH of both half cell will decrease

8. In the following electrochemical cell:

 $Zn | Zn^{2+} | | H^{\oplus} | (H_2) Pt$

 $E_{\text{cell}} = E_{\text{cell}}^{\odot}$. This will be when

(1) $[Zn^{2+}] = [H^{\oplus}] = 1 \text{ M and } p_{H_2} = 1 \text{ atm}$

(2) $[Zn^{2+}] = 0.01 \text{ M}, [H^{\oplus}] = 0.1 \text{ M}, \text{ and } p_{H_2} = 1 \text{ atm}$

(3) $[Zn^{2+}] = 1 \text{ M}, [H^{\oplus}] = 0.1 \text{ M}, \text{ and } p_{H_2} = 1 \text{ atm}$

(4) None of the above

9. For the electrochemical cell, (M | M^{\oplus}) \parallel (X^{\odot} | X),

For the electrochemical
$$E^{\ominus}(X \mid X^{\ominus}) = -0.33 \text{ V}$$
.
 $E^{\ominus}(M^{\oplus} \mid M) = 0.44 \text{ V}$, and $E^{\ominus}(X \mid X^{\ominus}) = -0.33 \text{ V}$.

From this data, one can conclude that

- (1) $M + X \longrightarrow M^{\oplus} + X^{\ominus}$ is the spontaneous reaction
- (2) $M^{\oplus} + X^{\odot} \longrightarrow M + X$ is the spontaneous reaction
- (3) $E_{\text{cell}}^{\odot} = 0.77 \text{ V}$
- (4) $E_{\text{cell}}^{\odot} = -0.77 \text{ V}$
- 10. The EMF of the following cell:

$$Cd(s) \mid CdCl_2(0.10 \text{ M}) \mid AgCl(s) \mid Ag(s)$$

is $0.6915 \,\mathrm{V}$ at $0^{\circ}\mathrm{C}$ and $0.6753 \,\mathrm{V}$ at $25^{\circ}\mathrm{C}$. The ΔH of reaction in kJ at 25°C is

- (1) 176
- (2) -234.7
- (3) 123.5
- (4) 167.6
- 11. In which of the following cells, EMF is greater than E^{\odot}_{cell} ?
 - (1) Pt, $H_2(g) \mid H^{\oplus}(pH = 5) \parallel H^{\oplus}(pH = 3) \mid H_2(g), Pt$
 - $(2) \ Zn(s) \ | \ Zn^{2+}(0.2 \ M) \ \| \ Cu^{2+}(0.1 \ M) \ | \ Cu(s)$
 - (3) $Cr(s) \mid Cr^{3+}(0.1 \text{ M}) \parallel Cu^{2+}(0.2 \text{ M}) \mid Cu(s)$
 - (4) Pt, $H_2(g) \mid H^{\oplus}$ (pH = 4) $\parallel H^{\oplus}$ (pH = 6) $\mid H_2(g) \mid Pt$
- 12. If A + B \rightleftharpoons C + D; $K_C = K_1$ and $E^{\odot} = a$ V

$$2A + 2B \rightleftharpoons 2C + 2D$$
; $K_C = K_2$ and $E^{\odot} = b \ V$

- (2) $K_2 = K_1^2$ (3) a = 2b (4) $b = a^2$ (1) a = b
- 13. Select the wrong relation(s).

(1)
$$\Delta S = \left(\frac{\partial E}{\partial T}\right)_P \times nF$$
 (2) $-\Delta S = \left(\frac{\partial E}{\partial T}\right)_P \times nF$

$$(2) - \Delta S = \left(\frac{\partial E}{\partial T}\right)_P \times nF$$

$$(3) \left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial \Delta S}{\partial T}\right)$$

(3)
$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial \Delta S}{\partial T}\right)$$
 (4) $\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta H + nEF}{T}$

- 14. Select the correct statement(s) about NHE.
 - (1) E^{\odot} of NHE is arbitrarily assumed to be zero.
 - (2) E^{\odot} of NHE is equal to zero.
 - (3) NHE refers as Pt, $H_2(g) | H^{\oplus}(aq)$ at 25°C.
 - (4) NHE is very susceptible to dissolved O2, H2S, and all other reducing agents.
- 15. In which of the following cells salt bridge is not needed?
 - $(1) \ Pb \ | \ PbSO_4(s) \ | \ H_2SO_4 \ | \ PbO_2(s) \ | \ Pb$
 - (2) Cd | CdO(s) | KOH(aq) | NiO $_{2}$ (s) | Ni
 - (3) Fe(s) | FeO(s) | KOH(aq), $Ni_2O_3(s)$ | Ni
 - (4) $Zn \mid ZnSO_4 \mid CuSO_4 \mid Cu$
- 16. Select the correct statements if 9.65 A current is passed for 1 hour through the cell:
 - Ag | Ag $^{\oplus}$ (1 M) || Cu $^{2+}$ (1 M) | Cu.
 - (1) Ag will oxidize to Ag^{\oplus} and new $[Ag^{\oplus}] = 1.36$ M.
 - (2) Ag^{\oplus} will reduce to Ag and new $[Ag^{\oplus}] = 0.64$ M.
 - (3) Cu^{2+} will reduce to Cu and new $[Cu^{2+}] = 0.82$ M.
 - (4) Cu will oxidize to Cu^{2+} and new $[Cu^{2+}] = 0.82$ M.
- 17. The temperature coefficient of the cell is $\left(\frac{\partial E}{\partial T}\right)_{B}$. Choose the correct statement(s).

- (1) When $\left(\frac{\partial E}{\partial T}\right)_{R} = 0$, then $\Delta H = -nF E$
- (2) When $\left(\frac{\partial E}{\partial T}\right)_{R} < 0$, then $|nFE| > |\Delta H|$
- (3) When $\left(\frac{\partial E}{\partial T}\right)_{R} > 0$, then $|nFE| < |\Delta H| \text{Exothern}_{i_{\mathbb{C}}}$ reaction
- (4) When $\left(\frac{\partial E}{\partial T}\right)_{D} = 0$, then $|\Delta H| > |nFE|$ Endothernic
- 18. Which of the following statements is/are correct?
 - (1) F₂ is the strongest oxidizing agent.
 - (2) Li is the strongest reducing agent.
 - (3) Li[⊕] is the weakest oxidizing agent.
 - (4) F₂ has a highest reduction potential.
- 19. For $I_2 + 2e^- \longrightarrow 2I^{\odot}$, standard reduction potential $= +0.54 \text{ V. For } 2\text{Br}^{\odot} \longrightarrow \text{Br}_2 + 2e^-, \text{ standard oxidation}$ potential = -1.09 V. For Fe \longrightarrow Fe²⁺ + 2e⁻, standard oxidation potential = +0.44 V. Which of the following reactions is(are) spontaneous?
 - $(1) Br_2 + 2I^{\odot} \longrightarrow 2Br^{\odot} + I_2$
 - (2) Fe + Br₂ \longrightarrow Fe²⁺ + 2Br $^{\odot}$
 - (3) Fe + $I_2 \longrightarrow Fe^{2+} + 2I^{\odot}$
 - (4) $I_2 + 2Br^{\odot} \longrightarrow 2I^{\odot} + Br_2$
- 20. Consider the cell:

Pt $| H_2(p_1 \text{ atm}) | H^{\oplus}(x, M) | H^{\oplus}(x, M) | H_2(p, atm) | Pt$ The cell reaction be spontaneous if

- (1) $p_1 = p_2$ and $x_1 > x_2$
- (2) $p_1 = p_2$ and $x_1 < x_2$
- (3) $x_1 = x_2$ and $p_1 > p_2$
- (4) $x_1 = x_2$ and $p_1 < p_2$
- 21. Which of the following changes will cause the free energy of a cell reaction to decrease?
 - $\operatorname{Zn} | \operatorname{ZnSO}_4(\operatorname{aq})(x_1 \operatorname{M}) | | \operatorname{HCl}(\operatorname{aq})(x_2 \operatorname{M}) / \operatorname{H}_2(g), \operatorname{Pt}$
 - (1) Increase in the volume of HCl solution from 100 mL to 200 mL
 - (2) Increase in the pressure of hydrogen from 1 atm to 2 atm
 - (3) Increase in molarity x_2 from 0.1 to 1 M
 - (4) Decrease in molarity x_1 from 1 M to 0.1 M
- 22. During the working of a galvanic cell and with the passage of time
 - (1) Spontaneity of the cell reaction decreases, E_{cell} decreases
 - (2) Reaction quotient Q decreases, E_{cell} increases
 - (3) Reaction quotient Q increases, E_{cell} decreases
 - (4) At equilibrium, $Q = K_{eq}$, $E_{cell} = 0$
- 23. In the following electrochemical cell: Pt | $H_2(x \text{ atm}) | H^{\oplus} (pH = y) || Zn^{2+}(z M) | Zn$ $E^{\odot}_{\text{cell}} = E_{\text{cell}}$. This will be possible when

(1) $[Zn^{2+}] = [H^{\oplus}] = 1 \text{ M and } p_{H_2} = 1 \text{ atm}$

(2) $[Zn^{2+}] = 0.01 \text{ M}, [H^{\oplus}] = 0.1 \text{ M}, \text{ and } p_{\text{H}_2} = 1 \text{ atm}$

(3) $[Zn^{2+}] = 1 \text{ M}, [H^{\oplus}] = 0.1 \text{ M}, \text{ and } p_{\text{H}_2} = 0.01 \text{ atm}$

(4) $[Zn^{2+}] = [H^{\oplus}] = 0.1 \text{ M} \text{ and } p_{\text{H}_2} = 0.1 \text{ atm}$

24. Consider the cell:

 $C_{Cd(s)} \mid Cd^{2+} (1.0 \text{ M}) \parallel Cu^{2+} (1.0 \text{ M}) \mid Cu(s)$

If we wish to make a cell with a more positive voltage using the same substances, we should

(1) Increase both $[Cd^{2+}]$ and $[Cu^{2+}]$ to 2.0 M

(2) Decrease the [Cd²⁺] to 0.1 M

(3) Increase the [Cu²⁺] to 2.0 M

(4) Decrease both the [Cd²⁺] and [Cu²⁺] to 0.01 M

25. Consider the following concentration cell:

 $\operatorname{\mathsf{Zn}}(s) \mid \operatorname{\mathsf{Zn}}^{2^+}(0.024\ M) \parallel \operatorname{\mathsf{Zn}}^{2^+}(0.480\ M) \mid \operatorname{\mathsf{Zn}}(s)$

Which of the following statements is(are) correct?

(1) The EMF of the cell at 25°C is nearly 0.038 V.

(2) The EMF of the cell at 25°C is nearly -0.038 V.

(3) If water is added in LHE, so that the [Zn²⁺] is reduced to 0.012 M, the cell voltage increases.

(4) If water is added in LHE, so that the [Zn²⁺] is reduced to 0.012 M, the cell voltage remains same.

26. Given: $H_2O_2 \longrightarrow O_2 + 2H^{\oplus} + 2e^ H_2O_2 + 2H^{\oplus} + 2e^- \longrightarrow 2H_2O$ $E^{\ominus} = 1.77 \text{ V}$ $E^{\odot} = -0.535 \text{ V}$ $I^{\odot} \longrightarrow I_{2} + 2e^{-}$

Which of the following statements is(are) correct?

(1) H_2O_2 behaves as an oxidant for I_2/I^{\odot} .

(2) $\rm H_2O_2$ behaves as an reductant for $\rm I_2/I^{\odot}$.

(3) $\rm I^{\odot}/I_{2}$ behaves as an reductant for $\rm H_{2}O_{2}.$

(4) None of these is correct.

27. Given:

 $E^{\odot} = 0.08 \text{ V}$ $A^{2+} + 2e^- \longrightarrow A(s)$ $E^{\odot} = -0.64 \text{ V}$ $B^{\oplus} + e^{-} \longrightarrow B(s)$ $E^{\odot} = 1.03 \text{ V}$ $X_2(g) + 2e^- \longrightarrow 2X^{\odot}$

Which of the following statements is/are correct?

(1) $X_2(g)$ will oxidize both (A) and (B).

(2) A²⁺ will oxidize B.

(3) The reaction

 $2X^{\odot} (1.0 \text{ M}) + A^{2+}(1.0 \text{ M}) \longrightarrow X_2(1 \text{ atm}) + A(s)$ will be spontaneous.

(4) The oxidizing power of A^{2+} , B^{\oplus} , and $X_2(g)$ is in the order $X_2 > A^{2+} > B^{\oplus}$.

Electrolysis

28. Peroxodisulphate salts (e.g., $Na_2S_2O_8$) are strong oxidizing agents used as bleaching agents for fats, oils, etc. Given:

 $O_2(g) + 4H^{\oplus}(aq) + 4e^- \longrightarrow 2H_2O(l)$ $E^{\odot} = 1$ $S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$ $E^{\odot} = 2$ Which of the following statements is(are) correct? $E^{\odot} = 1.23 \text{ V}$ $E^{\odot} = 2.01 \text{ V}$

(1) Oxygen gas can oxidize sulphate ion to per-oxo disulphate ion $(S_2O_8^{-2})$ in acidic solution.

(2) $O_2(g)$ is reduced to water.

(3) Water is oxidized to O_2 .

(4) $S_2O_8^{-2-}$ ions are reduced to SO_4^{-2-} ions.

29. A current is passed through 500 mL of an aqueous solution of CaI₂. After sometime, it is observed that 50 millimoles of I₂ have been formed. Which of the following statements is(are) correct?

(1) The number of faradays of charge passed through the solution is 0.10 F.

(2) The volume of dry H_2 at STP that has been formed during electrolysis is 1120 mL.

(3) The pH of the solution is nearly 0.7.

(4) The mass of calcium produced is 2.0 g.

30. During the electrolysis of aqueous zinc nitrate

(1) Zinc plates out at the cathode

(2) Zinc plates out at the anode

(3) Hydrogen gas H₂ is evolved at the anode

(4) Oxygen gas O2 is evolved at the anode

31. During electrolysis, O₂(g) is evolved at anode in

(1) Dilute H₂SO₄ with Pt electrode

(2) Aqueous AgNO₃ with Pt electrode

(3) Dilute H₂SO₄ with Cu electrode

(4) Fused NaOH with an Fe cathode and Ni anode

32. During electrolysis of aqueous CuBr₂ using Pt electrode,

(1) Br₂(g) is evolved at anode

(2) Cu(s) is deposited at cathode

(3) $Br_2(g)$ is evolved at anode and $H_2(g)$ at cathode

(4) H₂(g) is evolved at anode

33. A current of 2.68 A is passed for 1.0 hour through an aqueous solution of CuSO_4 using copper electrodes.

Which of the following statements is/are correct?

(1) Increase in the mass of cathode = 3.174 g

(2) Decrease in the mass of anode = 3.174 g

(3) No change in the mass of electrodes

(4) The ratio between the change in the mass of cathode to anode is 1:2

34. When 4.0 A of current is passed through a 1.0 L, 0.10 M Fe3+(aq) solution for 1.0 hour, it is partly reduced to Fe(s) and partly of Fe²⁺(aq). The correct statement(s) is(are):

(1) 0.10 mol of electrons are required to convert all Fe3+ to

(2) 0.025 mol of Fe(s) will be deposited.

(3) 0.075 mol of iron remains as Fe^{2+} .

(4) 0.050 mol of iron remains as Fe²⁺.

35. Electrolysis of aqueous solutions of which of the following substances results in only the decomposition of water?

(1) Potassium chloride

(2) Zinc sulphate

(3) Potassium hydroxide

(4) Sodium phosphate

3.104 Physical Chemistry

- **36.** When an aqueous solution of CaCl₂ is electrolyzed using inert electrodes, which of the following is(are) true?
 - (1) Calcium deposits on cathode
 - (2) Calcium deposits on anode
 - (3) Chlorine is liberated on anode
 - (4) Calcium hydroxide precipitates near cathode on prolonged hydrolysis
- 37. On passing 0.5 mol of electrons through CuSO₄ and Hg₂(NO₃)₂ solutions in series using inert electrodes
 - (1) 0.5 mol of Cu is deposited
 - (2) 0.5 mol of Hg is deposited
 - (3) 0.125 mol of O₂ is produced
 - (4) 0.5 mol of O₂ is produced
- 38. Which of the following statements is/are correct?
 - (1) The electrolysis of concentrated H₂SO₄ at 0–5°C using a Pt electrode produces H₂S₂O₈.
 - (2) The electrolysis of a brine solution produces NaClO₃ and NaClO.
 - (3) The electrolysis of a CuSO₄ solution using Pt electrodes causes the liberation of O₂ at anode and the deposition of copper at cathode.
 - (4) All electrolytic reactions are redox reactions.
- 39. If same quantity of electricity is passed through three electrolytic cells containing $FeSO_4$, $Fe_2(SO_4)_3$, and $Fe(NO_3)_3$, then
 - (1) The amount of iron deposited in FeSO₄ and Fe₂(SO₄)₃ are equal.
 - (2) The amount of iron deposited in FeSO₄ is 1.5 times of the amount of iron deposited in Fe(NO₃)₃
 - (3) The amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ are equal.
 - (4) The same amount of gas is evolved in all three cases of the anode.
- **40.** Which of the following aqueous solutions remain alkaline after electrolysis?
 - (1) CH₃COONa
- (2) KNO₃
- (3) NaCl
- (4) LiF
- **41.** A solution containing Na[®], NO₃[®], Cl[®], and SO₄²⁻ ions, all at unit concentrations, is electrolyzed between nickel anode and platinum cathode. As the current is passed through the cell
 - (1) pH of the cathode increases
 - (2) Oxygen is the major product at anode
 - (3) Nickel is deposited at cathode
 - (4) Chlorine is the major product at anode

Conductance, specific, equivalent and molar conductance

- 42. Which of the following statements is/are correct?
 - (1) The cell constant of an electrolytic cell is measured as the product: κR rather using l/a.

- (2) As an electrolytic solution is diluted, its conductance, equivalent conductance, and molar conductance, increase.
- (3) Kohlrausch's law may be applied to calculate molar conductance at infinite dilution for both weak and strong electrolytes.
- (4) Kohlrausch's law may also be applied at any concentration of the electrolyte.
- **43.** For a strong electrolyte, equivalent conductance increases slowly with dilution and can be expressed by the relationship.

$$\Lambda_{\rm m} = \Lambda_{\rm m}^{\circ} - A\sqrt{c}$$

Which electrolyte(s) have same value of A?

- (1) NaCl
- (2) CaCl₂
- (3) ZnCl₂
- $(4) \text{ MgSO}_{4}$
- **44.** Identify the correct statement(s):
 - (1) $\Lambda_{\rm m}$ increases with increase in temperature.
 - (2) $\Lambda_{\rm m}$ decreases with increase in concentration.
 - (3) Specific conductance increase with increase in concentration.
 - (4) Specific conductance decreases with increase in temperature.
- 45. To observe the effect of concentration on the conductivity, electrolytes of different natures are taken in two vessels A and B; A contains weak electrolyte, e.g., NH₄OH and B contains strong electrolyte, e.g., NaCl. In both containers, the concentration of respective electrolyte is increased and the conductivity observed:
 - (1) In A conductivity increases, in B conductivity decrease
 - (2) In A conductivity decreases while, in B conductivity decrease
 - (3) In both A and B conductivity increases
 - (4) In both A and B conductivity decreases

Commercial cell and corrosion

- **46.** Iron can be prevented from rusting by
 - (1) Connecting iron to more electropositive metal—a case of cathodic protection.
 - (2) Connecting iron to more electropositive metal—a case of anodic protection.
 - (3) Connecting iron to less electropositive metal—a case of anodic protection.
 - (4) Connecting iron to less electropositive metal—a case of cathodic protection.
- **47.** In the atmosphere of industrial smog, copper corrodes to form
 - (1) Basic copper carbonate
 - (2) Copper sulphide
 - (3) Basic copper sulphate
 - (4) Copper oxide
- 48. The tarnishing of silver ornaments in atmosphere is due to
 - (1) Ag_2O (2)
 - $(2) Ag_2S$
- (3) Ag_2CO_3 (4) Ag_2SO_4

- 49. Rusting of iron is catalyzed by
 - (1) H[⊕]
- (2) Dissolved CO₂ in water
- (3) 0,

- (4) Impurities present in Fe
- 50. During discharging of a lead storage battery
 - (1) The reaction at anode is Pb \longrightarrow Pb²⁺ + 2e
 - (2) The reaction taking place at cathode is $pb^{2+} + 2e^- \longrightarrow Pb$
 - (3) The overall reaction is

$$P_b + P_bO_2 + 4H^{\oplus} + 2SO_4^{2-} \longrightarrow 2P_bSO_4 + 2H_2O_4$$

(4) The reaction taking place at cathode is

$$PbO_2 + 4H^{\oplus} + 2e^- \longrightarrow Pb^{2+} + 2H_2O$$

- 51. Which of the following cells is/are rechargeable or secondary cell(s)?
 - (1) Ni-Cd cell
- (2) Mercury cell
- (3) Lead storage cell
- (4) Lithium battery
- 52. Which of the following statements regarding rusting of iron is/are correct?
 - (1) It takes place in moist air.
 - (2) It is stopped in CO₂ atmosphere.
 - (3) It produces Fe (III) oxide.
 - (4) It is an electrochemical process.
- 53. Which of the following statements is/are incorrect?
 - (1) Rust is Fe₂O₃.
 - (2) Zn-Cu cell is called Daniell cell.
 - (3) Saline water slows down rusting.
 - (4) Pure metals undergo corrosion faster than impure metals.

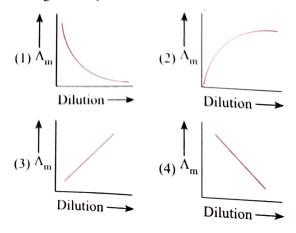
Miscellaneous

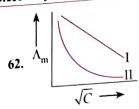
- 54. The oxidation potential of hydrogen half-cell will be negative if:
 - (1) $p(H_2) = 1$ atm and $[H^{\oplus}] = 1M$
 - (2) $p(H_2) = 1$ atm and $[H^{\oplus}] = 2$ M
 - (3) $p(H_2) = 0.2$ atm and $[H^{\oplus}] = 1$ M
 - (4) $p(H_2) = 0.2$ atm and $[H^{\oplus}] = 0.2$ M
- 55. Which of the following arrangement will produce oxygen at anode during electrolysis?
 - (1) Dilute H₂SO₄ with Pt electrodes
 - (2) Fused NaOH with inert electrodes
 - (3) Dilute H₂SO₄ with Cu electrodes
 - (4) Concentrated aq. NaCl with Pt electrodes
- 56. Which of the following are concentration cells?
 - $^{(1)}\,Pt\,|\,H_{2}(g)\,|\,HCl\,|\,H_{2}(g)\,|\,Pt$
 - (2) Cd, (Hg) | Cd^{2+} | (Hg), Cd a_1 (c)
 - $\overset{\text{(3)}}{Z} \underset{c_1}{Z} n(s) \mid \overset{}{Z} n^{2+} \parallel \overset{}{C} \underset{c_2}{u^{2+}} \mid \overset{}{C} u$

- (4) $Ag \mid AgCl \mid \underset{c_1}{Cl^{\Theta}}(aq) \parallel \underset{c_2}{Br^{\Theta}}(aq) \mid AgBr \mid Ag$
- 57. In electrolyte concentration cell:
 - (1) The electrode material and the solution in both halfcells are composed of the same substances
 - (2) Only the concentration of solutions of the same substances is different
 - (3) $E_{\text{cell}}^{\circ} = 0$
 - (4) The Nernst equaton reduces of

$$E_{\text{cell}} = -\left(\frac{0.0591}{n}\right) \log Q \text{ at } 25^{\circ}\text{C}$$

- **58.** Which is/are correct statement?
 - (1) No corrosion takes place in vacuum
 - (2) Corrosion is protected by electroplating
 - (3) During rusting Fe₂O₃. xH_2O is formed
 - (4) In presence of electrolyte, corrosion takes place with greater rate
- 59. 1000 mL 1M CuSO₄(aq) is electrolysed by 9.65 A current for 100 sec using Pt-electrode. Which is/are correct statement?
 - (1) Blue colour intensity decreases during electrolysis.
 - (2) Blue colour intensity remains constant if Cu-electrode is used.
 - (3) pH of solution is 8 after electrolysis.
 - (4) 28 mL of CH₄ at 1 atm and 273 K required for its combustion by O₂, liberated during electrolysis.
- 60. An ion travels 0.4 cm in 1 minute under the influence of 2 volt potential difference when electrodes are 3 cm apart. Which one are correct?
 - (1) Speed of ion = 6.67×10^{-3} cm s⁻¹
 - (2) Ionic mobility = 1×10^{-6} m² volt⁻¹ sce⁻¹
 - (3) Ionic mobility = 1.0×10^{-3} cm² volt⁻¹ sec⁻¹
 - (4) Ionic mobility = 4.44×10^{-3} cm² volt⁻¹ sec⁻¹
- 61. Which of the following graph incorrectly represents the variation of molar conductance ($\Lambda_{\rm m}$) with dilution for a strong electrolyte?





Above plot represents the variation of molar conductance against \sqrt{C} (where C = molar concentration of theelectrolyte). Select the incorrect options among the following:

- (1) Both I and II are for strong electrolyte
- (2) Both I and II are for weak electrolyte
- (3) I is for strong electrolyte and II for weak electrolyte
- (4) I is for weak electrolyte and II for strong electrolyte
- 63. The electrode potential of a glass electrode does not depend upon:
 - (1) Concentration of chloride ions
 - (2) Concentration of hydrogen ions
 - (3) Concentration of KCl solution
 - (4) All of these
- 64. A sample of water has a hardness expressed as 77.5 ppm Ca2+. This sample is passed through an ion exchange column and the Ca2+ is replaced by H[⊕]. Select the correct statement(s)
 - (1) pH of the water after it has been so treated is 2.4
 - (2) Every Ca²⁺ ion is replaced by one H[⊕] ion
 - (3) Every Ca²⁺ ion is replaced by two H[⊕] ions
 - (4) pH of the solution remains unchanged
- 65. In the electrolysis of a 40-L CuSO₄ solution, there are two possible reactions at anode:

i.
$$Cu \longrightarrow Cu^{2+} + 2e^{-}$$

ii.
$$2H_2O \longrightarrow 4H^{\oplus} + 4e^- + O_2$$

A current of 1.07 A is passed for 2 hours. The loss in the mass of Cu at anode was 1.27 g.

(Atomic weight of $Cu = 63.5 \text{ g mol}^{-1}$).

Which of the following statement(s) is/are correct?

- (1) 0.08 mol of electrons are passed through the solution during entire electrolysis.
- (2) 224 mL of O₂(g) is liberated at STP at anode.
- (3) Fraction of current in the production of Cu²⁺ ions = 0.5.
- (4) pH drops to 3.

Linked Comprehension Type

Paragraph 1

An aqueous solution containing 0.01 M Fe^{3+} and 0.01 M Fe^{2+} was titrated with a concentrated solution of NaOH at 30°C, so that changes in volumes were negligible. Assuming that the new species formed during titration are Fe(OH)₃ and Fe(OH)₂ only.

Given
$$E^{\odot}_{Fe^{3+}|Fe^{2+}} = 0.80 \text{ V}$$
,

Given
$$E_{\text{Fe}^{3+}|\text{Fe}^{2+}|}^{\text{Given }} = 10^{-37}$$
, and $K_{\text{sp Fe}(\text{OH})_2} = 10^{-19}$
 $K_{\text{sp Fe}(\text{OH})_3} = 10^{-37}$, and $K_{\text{sp Fe}(\text{OH})_2} = 10^{-19}$

- 1. Calculate the redox potential of Fe³⁺ | Fe²⁺ electrode at pH = 2(3) 0.2 V (4) 0.1 V
 - (2) 0.5 V (1) 0.8 V
- 2. The redox potential of Fe³⁺ | Fe²⁺ electrode at pH =4 $_{ig}$ (3) 0.2 V(4) 0.1 V(2) 0.5 V
- (1) 0.8 V3. The redox potential of Fe^{3+} | Fe^{2+} electrode at pH = 6 is
 - (3) 0.2 V(4) 0.1 V(2) 0.5 V (1) 0.8 V

Paragraph 2

4. Calculate $\Delta_{\mathsf{r}}G^{\ominus}$ of the reaction:

$$Ag^{\oplus}(aq) + Cl^{\ominus}(aq) \longrightarrow AgCl(s)$$

Given:
$$\Delta_f G^{\odot}_{AgCl} = -109 \text{ kJ mol}^{-1}$$

$$\Delta_{\mathbf{f}} G^{\odot}_{(\mathrm{Cl}^{\odot})} = -129 \text{ kJ mol}^{-1}$$

$$\Delta_{\rm f} G^{\odot}_{\rm (Ag^{\oplus})} = -77 \text{ kJ mol}^{-1}$$

- $(1) 97 \text{ kJ mol}^{-1}$
- $(2) -57 \text{ kJ mol}^{-1}$
- (3) 57 kJ mol⁻¹
- (4) 97 kJ mol⁻¹
- **5.** E_{cell}^{Θ} of the reaction above in Q. 4. is
 - (1) 0.59 V
- (2) -0.59 V
- (3) 0.295 V
- (4) -0.295 V
- **6.** $K_{\rm sp}$ of AgCl is
 - $(1)\ 10^{-13}$
- $(2)\ 10^{-12}$
- $(3)\ 10^{-11}$
- $(4) 10^{-10}$
- 7. 6.537×10^{-2} g of metallic Zn was added to 100 mL of

saturated solution of AgCl. Calculate $\log \frac{[Zn^{2+}]}{[A\alpha^{\oplus}]^2}$

Given: $E^{\odot}_{Ag^{\bigoplus} | Ag} = 0.80 \text{ V}, E^{\odot}_{Zn^{2+} | Zn} = -0.763 \text{ V}.$

 $K_{\rm sp}$ of AgCl $\approx 10^{-10}$; atomic weight of Zn = 65.37

- (1) 26.5
- (2) 13.24
- (3)53
- 8. Calculate the number of moles of Ag formed above in Q. 7.
 - $(1)\ 10^{-4}$
- $(2)\ 10^{-5}$
- $(3)\ 10^{-6}$
- $(4) 10^{-7}$

Paragraph 3

Fuel cells: Fuel cells are galvanic cells in which the chemical energy of fuel is directly converted into electrical energy. A type of fuel cell is a hydrogen-oxygen fuel cell. It consists of two electrodes made up of two porous graphite impregnated with a catalyst (platinum, silver, or metal oxide). The electrodes are placed in aqueous solution of NaOH. Oxygen and hydrogen are continuously fed into the cell. Hydrogen gets oxidized to H[®] which is neutralized by OH, i.e., anodic reaction.

$$H_2 \Longrightarrow 2H^{\oplus} + 2e^{-}$$

$$2H^{\oplus} + 2OH \Longrightarrow 2H_2O$$

$$H_2 + 2OH \Longrightarrow 2H_2O + 2e^{-}$$

At cathode, O_2 gets reduced to $\stackrel{\odot}{\mathrm{OH}}$

IV. Ag[⊕]

$$_{i.c.}O_2 + 2H_2O + 4e^- \Longrightarrow 4OH$$
 $_{Hence}$, the net reaction is $2H_2 + O_2 \Longrightarrow 2H_2O$
 $_{The overall reaction has}$
 $_{M} = -285.6 \text{ kJ mol}^{-1}$ and $\Delta G = -237.4 \text{ kJ mol}^{-1}$ at 25°C

 $_{Q. \text{ If the cell voltage is 1.23 V for the H}_2 \longrightarrow O_2 \text{ fuel cell and for the cell voltage}$

the half cell:

$$0_2 + 2H_2O + 4e^- \Longrightarrow 4OH \text{ has } E^{\odot} = 0.40 \text{ V},$$

 $0_2 + 2H_2O + 2e^- \Longrightarrow H_2 + 2OH \text{ will be}$
then E^{\odot} for $2H_2O + 2e^- \Longrightarrow H_2 + 2OH \text{ will be}$

then
$$E^{\odot}$$
 for $2H_2O + 2e^{-}$ \rightleftharpoons $H_2 + 2OH$ will be $H_2 +$

₁₀, What is the value of ΔS^{\odot} for the fuel cell at 25°C?

(1)-1600 J K⁻¹

 $(2) - 160 \text{ J K}^{-1}$

(3) 160 J K⁻¹

(4) 1600 J K^{-1}

11. Suppose the concentration of hydroxide ion in the cell is doubled, then the cell voltage will be

(1) Reduced by half

(2) Increased by a factor of 2

(3) Increased by a factor of 4

(4) Unchanged

12. A fuel cell is

- I. A voltaic cell in which continuous supply of fuels are sent at anode to perform oxidation.
- II. A voltaic cell in which fuels such as: CH4, H2, and CO are used up at anode.
- III. One which involves the reaction of H_2 – O_2 fuel cell such

Anode:
$$2H_2 + 4\overset{\odot}{O}H \longrightarrow 4H_2O(1) + 4e^-$$

Cathode: $O_2 + 2H_2O(1) + 4e^- \longrightarrow 4\overset{\odot}{O}H$

IV. The efficiency of H_2 – O_2 fuel cell is 70 to 75%.

(1) L, III

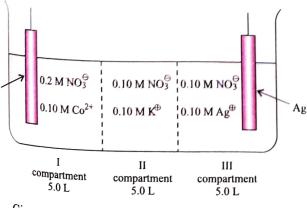
(2) I, III, IV

(3) I, II, III, IV

(4) I, II, III

aragraph 4

as shown below, consists of three compartments separated $\rlap/$ porous pots. The first contains a cobalt electrode in 5.0 L of 0.10 (Co(NO₃)₂; the second contains 5.0 L of 0.10 M KNO₃; the third ontains an Ag electrode in 5.0 L of 0.10 M AgNO₃. Assuming current with in the cell is carried equally by the negative and ositive ions by passing 0.1 F of electricity.



Given: $Co^{2+} + 2e^{-} \longrightarrow Co$

 $E^{\odot} = -0.28 \text{ V}$

$$Ag^{\oplus} + e^{-} \longrightarrow Ag$$
 $E^{\ominus} = 0.80 \text{ V}$
 $2Ag^{\oplus} + Co \longrightarrow Co^{2+} + 2Ag$ $E^{\ominus}_{cell} = 1.08 \text{ V}$

13. Finally, the I compartment contains

I. Co²⁺

II. NO₃[©]

III. K⊕

(1)I

(2) I, II

(3) I, II, III

(4) II, III, IV

14. Finally, the II compartment contains

(1)I

(2) I, II

(3) I, II, III

(4) II, III, IV

15. Finally the III compartment contains

(1)I

(2) I, II

(3) I, II, III

(4) II, III, IV

16. The final concentration of Co²⁺ in I, II, and III compartment is

(1) 0.105, 0.005, 0.0 M

(2) 0.005, 0.105, 0.0 M

(3) 0.105, 0.0, 0.005 M

(4) 0.0, 0.005, 0.105 M

17. The final concentration of NO_3^{\odot} in I, II, and III compartment is

(1) 0.100, 0.210, 0.0900 M

(2) 0.210, 0.100, 0.0900 M

(3) 0.0900, 0.210, 0.100 M 18. The final concentration of K^{\oplus} in I, II, and III compartment is

(4) 0.0900, 0.100, 0.210 M

(1) 0.090, 0.0, 0.0100 M

(2) 0.0, 0.0100, 0.090 M

(3) 0.0, 0.090, 0.0100 M

(4) 0.100, 0.090, 0.0 M

19. The final concentration of Ag^{\oplus} in I, II, and III compartment is

(1) 0.0, 0.0, 0.08 M

(2) 0.0, 0.08, 0.0 M

(3) 0.08, 0.0, 0.0 M

(4) 0.0 M in all compartments

Matrix Match Type



This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

	Column I		Column II
	Electric unit		Single unit
a.	Volt-ampere and joule second ⁻¹	p.	Coulomb
b.	Ampere-second and joule volt ⁻¹	q.	Ohm
c.	Volt ampere ⁻¹ and joule ampere ⁻² second ⁻¹	r.	Volt
d.	Joule ampere ⁻¹ second ⁻¹	s.	Watt
e.	Watt ampere ⁻¹ ohm ⁻¹	t.	Ampere

	Column I		Column II
	Properties		Units
a.	Cell constant	p.	$\Omega^{-1}\mathrm{cm}^2\mathrm{eq}^{-1}$
b.	Molar conductance	q.	cm ⁻¹ or m ⁻¹
c.	Equivalent conductance	r.	S cm ² mol ⁻¹
d.	Specific conductance	s.	mho
e.	Conductance	t.	mho cm ⁻¹
f.	Resistance	+	Ω

•	Column I		Column II
	Name of cell/battery		Electrolyte
a.	Mercury cell	p.	KOH solution
b.	Lead storage battery	q.	HgO + KOH (moist)
c.	Dry cell	r.	38% H ₂ SO ₄

d.	Fuel cell (H ₂ –O ₂)		MnO ₂ + C(touching cathode) and paste of NH ₄ Cl + ZnCl ₂ (touching anode)
e.	Ni-Cd storage cell	t.	Concentrated aqueous KOH solution

	Column I		Column II
	Concentration of cell at 30° C (Take $2.303 RT/F = 0.06$)		$E_{ m cell}$
a.	Pt $H_2(g)(1 \text{ atm})$ $CH_3COOK (10^{-1} \text{ M}) + CH_3COOH (10^{-2} \text{ M}) pK_{a(CH_3COOH)} = 4.74$ $(NH_4)_2SO_4(0.2 \text{ M}) + NH_4OH (0.2M) pK_{b NH_4OH} = 4.74 H_2(g)(1 \text{ atm}) Pt$	p.	- 0.03 V
b.	$Cu(s) \mid Cu^{2+}(1 \text{ M}) \parallel Cu^{2+}(0.1 \text{ M}) \mid Cu(s)$	q.	0.2178 V
c.	$ Pt \mid Cl_{2}(g) \ (1 \ atm) \mid Cl^{\Theta}(10^{-2} \ M) \parallel Cl^{\Theta}(10^{-3} \ M) \mid Cl_{2}(g) \ (2 \ atm) \mid Pt $	r.	-0.1932 V
d.	$ \begin{array}{l} \text{Pt} \mid \text{H}_2(\text{g}) \; (1 \; \text{atm}) \mid \text{NH}_4\text{OH} (10^{-2} \; \text{M}) \; \text{p} \\ K_b = 4.74 \; \text{pK}_3\text{COONH}_4 \; \text{p} \\ K_a \; \text{CH}_3\text{COOH} \\ = 4.74 \; \text{pK}_b \; \text{NH}_4\text{OH} = 4.74 \; \; \text{H}_2(\text{g}) \; (1 \; \text{atm}) \; \; \text{Pt} \\ \end{array} $	s.	0.1 V
e.	Glass electrode Buffer solution pH = 6 Standard calomel electrode Given: $E_{\text{SCE}} = 0.24 \text{ V}$; $E_{\text{glass}}^{\odot} = 0.5 \text{ V}$	t.	0.069 V

	Column I		Column II
	Electrolysis	ALCONOMIC STATES	pH and products at anode and cathode
	Electrolysis of 100 L aqueous solution of CH ₃ COOK by passing 2 F of electricity	p.	pH = 12.3 Anode = Ethane(g) + $CO_2(g)$ Cathode = $H_2(g)$
	Electrolysis of 10 L aqueous solution of HCOOK by passing 1 F of electricity.	q.	pH = 13.0 Anode = $H_2(g) + CO_2(g)$ Cathode = $H_2(g)$
	Electrolysis of 10 L aqueous solution of K ₂ SO ₄ by passing 1 F of electricity.	r.	$pH = 7.0$ $Anode = O_2(g)$ $Cathode = H_2(g)$
u,	Electrolysis of 10 L aqueous solution of CuF ₂ by passing 1 F of electricity	s.	pH = 1.0 Anode = O ₂ (g) Cathode = Cu(g)

	Column I		
	Cell and EMF		Column II
a.	Pt H ₂ (1 atm) H ^{\oplus} (10 ⁻³ M) H ^{\oplus} (10 ⁻⁶ M) H ₂ (1 atm) Pt		Characteristics
	$ \mathcal{L}_{\text{cell}} = 0.177 \text{ V}$	p.	Spontaneous
b.	Pt $F_2(g)$ (1 atm) F^{Θ} (10 ⁻² M) F^{Θ} (10 ⁻³ M) $F_2(g)$ (2 atm) Pt		
	Cell 0.000 V	q.	Non-spontaneous
c.	Hg, $Hg_2Cl_2(s) \mid KCl$ (saturated solution) $\parallel H^{\oplus}(pH = 10) \mid Q$, $QH_2 \mid Pt$		
	Cell Size 0.24	r.	Exergonic
	$E_{\rm Q H_{\rm 2Q}} = 0.7\rm V$		
d.	$Q + 2H^{\oplus} (pH = 2) + 2e^{-} \longrightarrow H_2Q(s)$		9
	$E_{\text{cell}}^{\ominus} = 0.7 \text{ V}, E_{\text{cell}} = 0.582 \text{ V}$	s.	Endergonic

Q.7 to Q.10: Answer the question given below by appropriately matching the information given in three column of the following

Compounds and their ionic equ	ivalent and molar conductivities	1 2 7			
lonic equivalent conductivities (S cm ² Eq ⁻¹)	Ionic molar conductivities (S cm ² mol ⁻¹)	64.9	$\stackrel{\circ}{\Lambda}_{eq}$ of compound (S cm 2 Eq $^{-1}$)		$\stackrel{\circ}{\Lambda}_{\rm m}$ of compound (S cm ² mol ⁻¹)
Potash alum: K^{\oplus} , Al ⁺³ and $SO_4^{2-} = x$, y, and z respectively	K^{\oplus} , Al ⁺³ and $SO_4^{2-} = x'$, y' , and z' respectively	i	$\left(\frac{x}{4} + \frac{3y}{4} + z\right)$	p	(x'+y'+z')
Sodium potassium oxalate: K^{\oplus} , Na^{\oplus} and $C_2O_4^{2-} = x$, y, and z respectively	K^{\oplus} , Na^{\oplus} and $C_2O_4^{2-} = x'$, y' , and z' respectively	ii	$\left(x + \frac{y}{4} + \frac{3z}{4}\right)$	q	(2x'+2y'+4z')
Mohr's salt: SO_4^{2-} , NH_4^{\oplus} and $Fe^{+2} = x$, y, and z respectively	SO_4^{2-} , NH_4^{\oplus} and $Fe^{+2} = x'$, y' , and z' respectively	iii	$\left(\frac{x}{2} + \frac{y}{2} + z\right)$	r	(4x'+y'+2z')
Pseudo alum: SO_4^{2-} , $Fe+^2$ and $AI^{+3} = x$, y , and z respectively	SO_4^{2-} , Fe^{+2} and $Al^{+3} = x'$, y' and z' respectively	iv	$\left(x+\frac{y}{2}+\frac{z}{2}\right)$	S	(2x'+y'+z')

- 7. For potash alum, the correct combination is:
 - (1) a—i—q
- (2) a—iii—p
- (3) a—iv—s
- (4) a—ii—r
- 8. For sodium potassium oxalate, the correct combination is:
 - (1) b—i—q
- (2) b—iii—p
- (3) b—iv—s
- (4) b—ii—r
- 9. For Mohr's salt, the correct relation between $\mathring{\Lambda}_{\rm eq}$ and $\mathring{\Lambda}_{\rm m}$

(1) Value in (ii) =
$$\left(\frac{\text{value in } p}{8}\right)$$

(2) Value in (iv) =
$$\left(\frac{\text{value in s}}{8}\right)$$

(3) Value in (ii) =
$$\left(\frac{\text{value in } p}{4}\right)$$

(4) Value in (iv) =
$$\left(\frac{\text{value in s}}{4}\right)$$

10. For pseudo alum, the correct relation between $\mathring{\Lambda}_{eq}$ and $\mathring{\Lambda}_{m}$

(1) Value in (ii) =
$$\left(\frac{\text{value in } p}{2}\right)$$

(2) Value in (iv) =
$$\left(\frac{\text{value in r}}{8}\right)$$

(3) Value in (ii) =
$$\left(\frac{\text{value in p}}{8}\right)$$

(4) Value in (iv) =
$$\left(\frac{\text{value in } r}{2}\right)$$

Numerical Value Type



1. What is the total score for the correct statement(s) from the following?

	Statement	Score
a.	A stronger oxidizing agent has lower oxidation potential.	4
b.	Solution of aqueous AgNO ₃ cannot be stored in Zn vessel.	1
c.	In a concentration cell made up of Ag electrodes, the one having [Ag [⊕]] will behave as cathode.	3
d.	[Cu ²⁺] will remain constant during electrolysis of aqueous CuSO ₄ solution with Pt electrode as anode and Cu electrode as cathode.	2

- 2. During the electrolysis of conc H₂SO₄, it was found that H₂S₂O₈ and O₂ were liberated in a molar ratio of 3:1. How many moles of H₂ were found in terms of moles of H₂S₂O₈? (Express your answer as: 3 × moles of H₂)
- 3. How many Faradays are required to reduce 1 mol of BrO₃[⊙] to Br[⊙] in basic medium?
- 4. The total number of Faradays required to oxidize the following separately:
 - a. 1 mol of S₂O₃²⁻ in acid medium
 - b. 1 Equivalent of S₂O₃²⁻ in neutral medium
 - c. 1 mol of S₂O₃²⁻ in basic medium.
- 5. For the oxidation of ferric oxalate to CO₂, 18 F of electricity is required. How many moles of ferric oxalate is oxidized?

- 6. During the discharge of a lead storage battery, the density of 40% H₂SO₄ by weight fell from 1.225 to 0.98 (which is 20% by weight). What is the change in molarities of H₂SO₄?
- 7. In Q. 6 above, the number of ampere hours for which the battery is used containing 1 L of the acid is 16.08x ampere hour. Calculate the value of x.
- **8.** ΔG for the reaction:

$$\frac{4}{3}$$
 Al + O₂ $\longrightarrow \frac{2}{3}$ Al₂O₃

is
$$-772$$
 kJ mol⁻¹ of O_2 .

Calculate the minimum EMF in volts required to carry out an electrolysis of Al₂O₃.

9. What is the total score for the correct statement(s) from the following.

Given:
$$MnO_4^{\odot} + 8H^{\oplus} + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
; $E^{\odot} = 1.51 \text{ V}$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$
;

$$E^{\odot} = 0.77 \text{ V}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^{\odot};$$

$$E^{\odot} = 1.36 \text{ V}$$

$$Ce^{4+} + e^{-} \longrightarrow Ce^{3+}$$
:

$$E^{\odot} = 1.76 \text{ V}$$

	Statement	Score
a .	MnO_4^{\odot} is a sufficiently strong oxidant in acidic solution (pH = 0) to oxidize Fe ²⁺ ion.	1
b.	Fe^{2+} ion cannot be titrated against standard $KMnO_4$ solution if the medium is made acidic (pH = 0) by adding HCl.	2
c.	$\mathrm{MnO_4}^{\odot}$ ion cannot oxidize $\mathrm{Ce^{3+}}$ in acidic medium (pH = 0).	3
d.	Fe ²⁺ cannot be titrated against standard KMnO ₄ solution in acidic medium (pH = 0) in the presence of Ce ³⁺ ion.	4

10. What is the total score for the correct statement(s) from the following

Given:
$$E_{\text{Li}\oplus | \text{Li}}^{\odot} = -3.05 \text{ V}$$

$$E^{\Theta}_{\text{Na} \oplus | \text{Na}} = -2.71 \text{ V}$$

$$E^{\odot}_{K^{\oplus}|K} = -2.93 \text{ V}$$

Alkali metals react with water according to the following reaction (M = Alkali metals):

$$2M + H_2O \longrightarrow 2MOH + H_2$$

It is found that Li reacts gently with water, whereas K reacts violently with water.

	Statement	Score
a.	ΔG values have nothing to do with kinetics of the reaction.	4
b.	The metal having large standard oxidation potential will have lesser reactivity.	3
c.	Potassium (K) has low melting point and heat of reaction which is sufficient to make it melt or even vapourize. This leads to exponential increase in its surface area.	2
d.	The ionization potential of K is smaller than that of Li.	1

11. When electrolysis of KCl is done in alkaline medium. 10 g of KClO₃ is produced as follows:

$$Cl^{\odot} + 6\overset{\odot}{O}H \longrightarrow ClO_3^{\odot} + 3H_2O + 6e^{-}$$

A current of 2A is passed for 10.941 hours. Calculate the Percentage current efficiency used in the process.

 $(Mw \text{ of KClO}_3 = 122.5)$

Archives

JEE MAIN

Single Correct Answer Type

1. Given,
$$E_{Fe^{3+}/Fe}^{\circ} = -0.036 \text{ V}$$

$$E_{\text{Fe}^{2a}/\text{Fe}}^{\circ} = -0.439 \text{ V}$$

The value of standard electrode potential for the charge,

$$Fe^{3+}(aq.) + e^{-} \longrightarrow Fe^{2+}(aq.)$$
 will be

2. The Gibbs energy for the decomposition of Al₂O₃ at 500°C

$$\frac{2}{3}$$
 Al₂O₃ $\longrightarrow \frac{4}{3}$ Al + O₂ $\Delta_r G = +966$ kJ mol⁻¹

The potential difference needed for electrolytic reduction of Al₂O₃ at 500°C is at least

3. The reduction potential of hydrogen half-cell will be negative if

(1)
$$p(H_2) = 1$$
 atm and $[H^+] = 2.0 \text{ M}$

(2)
$$p(H_2) = 1$$
 atm and $[H^+] = 1.0 \text{ M}$

(3)
$$p(H_2) = 2$$
 atm and $[H^+] = 1.0$ M

(4)
$$p(H_2) = 2$$
 atm and $[H^+] = 2.0 \text{ M}$

(AIEEE 2011)

- 4. Resistance of 0.2 M solution of an electrolyte is 50 \(\text{D} \) The specific conductance of the solution is 1.3 S m resistance of the solution is 1.3 S m resistance of the 0.4M solution of the same electrolyte is 260 O its mod 260 Ω , its molar conductivity is
 - (1) 6250 S m² mol⁻¹
 - (2) $6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
 - (3) $625 \times 10^{-4} \text{ S nn}^2 \text{ mol}^{-1}$
 - (4) 62.5 S m² mol⁻⁻¹

(AIEEE 2011)

- 5, The standard reduction potentials for Zn²⁺/Zn, Ni²⁺/Ni and The standard -0.76, -0.23 and -0.44 V, respectively. The reaction $X + Y^{2+} + Y$ will be spontaneous when (2) X = Ni, Y = Zn
 - (1) X = Ni, Y = Fe

- (4) X = Zn, Y = Ni
- (3) X = Fe, Y = Zn

(AIEEE 2012)

6. Given,
$$E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} = -0.74 \text{ V}$$
; $E_{\text{MnO}_3/\text{Mn}^{2+}}^{\circ} = 1.51 \text{ V}$

$$E_{\text{Cr}_2\text{O}_7^2/\text{Cr}_3^{3+}}^{\circ} = 1.33 \text{ V}; E_{\text{Cr}/\text{Cr}_7}^{\circ} = 1.36 \text{ V};$$

Based on the data given above, strongest oxidizing agent will be

(1) Cl

(2) Cr^{3+}

(3) Mn²⁺

 $(4) \text{ MnO}_4^-$

(JEE Main 2013)

- 7. Resistance of 0.2 M solution of an electrolyte is 50 Ω . The specific conductance of the solution is 1.4 S m⁻¹. The resistance of 0.5 M solution of the same electrolyte is 280 Ω . The molar conductivity of 0.5 M solution of the electrolyte in S mol-1 is
 - (1) 5×10^{-4}
- (2) 5×10^{-3}
- (3) 5×10^3
- (4) 5×10^2

(JEE Main 2014)

- & The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_c and λ_o is given as
 - (1) $\lambda_c = \lambda_o + (B)C$
- (2) $\lambda_c = \lambda_o (B)C$
- (3) $\lambda_c = \lambda_o (B) \sqrt{C}$
- $(4) \ \lambda_c = \lambda_o + (B) \sqrt{C}$

(JEE Main 2014)

- 9. In which of the following reactions H_2O_2 acts as a reducing agent?
 - (1) $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$
 - (2) $H_2O_2 2e^- \longrightarrow O_2 + 2H^+$
 - (3) $\text{H}_2\text{O}_2 + 2e^- \longrightarrow 2\text{HO}^-$
 - (4) $H_2O_2 + 2OH^- 2e^- \longrightarrow O_2 + 2H_2O$
 - (1) 1, 2

(2) 3, 4

(3) 1.3

- (JEE Main 2014) (4) 2, 4
- 10. The metal that cannot be obtained by the electrolysis of an aqueous solution of its salts is
 - (1) Ag

(2) Ca

(3) Cu

- (JEE Main 2014) (4) Cr
- 11. Given below are the half-cell reactions

$$Mn^{2+} + 2e^{-} \longrightarrow Mn$$
, $E^{\circ} = -1.18 \text{ V}$
 $2(Mn^{3+} + e^{-} \longrightarrow Mn^{2+})$, $E^{\circ} = +1.51 \text{ V}$

The E° for 3 Mn²⁺ \longrightarrow Mn + 2Mn³⁺ will be

- (1) -2.69V, the reaction will not occur
- (2) -2.69 V the reaction will occur
- (3) -0.33 V, the reaction will not occur
- - (JEE Main 2014)
- (4) -0.33 V, the reaction will occur 12. Two faraday of electricity is passed through a solution of CuSO₄. The mass of copper deposited at the cathode is: (at. mass of Cu = 63.5 amu)

(1) 0 g

(2) 63.5 g

(3) 2g

- (4) 127 g (JEE Main 2015)
- 13. Galvanization is applying a coating of
 - (1) Zn

(2) Pb

(3) Cr

- (JEE Main 2016) (4) Cu

14. Given

$$E_{\text{Cl}_2/\text{Cl}^-}^o = 1.36\text{V}, E_{\text{Cr}^{3*}/\text{Cr}}^o = -0.74\text{V}$$

$$E_{\text{Cr}_2\text{O}_7^{2^-}/\text{Cr}^{3^+}}^o = 1.33\text{V}, E_{\text{MnO}_4^-/\text{Mn}^{2^+}}^o = 1.51\text{V}$$

Among the following the strongest reducing agent is:

(1) Cr

(2) Mn^{2+}

 $(3) Cr^{3+}$

- (JEE Main 2017) (4) Cl⁻
- 15. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane?

(Atomic weight of B = 10.8 u)

- (1) 0.8 hours
- (2) 3.2 hours
- (3) 1.6 hours
- (4) 6.4 hours

(JEE Main 2018)

JEE ADVANCED

Single Correct Answer Type

1. Consider the following cell reaction:

Consider the following central
$$2Fe(s) + O_2(g) + 4H^{\oplus}(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$E^{\odot} = 1.67 \text{ V}$$

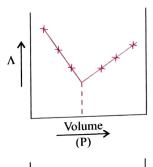
At
$$[\text{Fe}^{2+}] = 10^{-3} \text{ M}$$
, $p(O_2) = 0.1 \text{ atm and pH} = 3.$

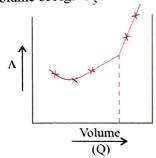
The cell potential at 25°C is

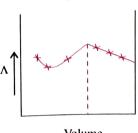
- (1) 1.47 V
- (2) 1.77 V
- (3) 1.87 V
- (4) 1.57 V

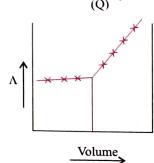
(IIT-JEE 2010)

2. AgNO₃(aq) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (A) versus the volume of AgNO3 is









Volume

(2) Q

(1) P

- (3) R
 - - (4) S
 - (IIT-JEE 2011)

3. The standard reduction potential data at 25°C is given below:

$$E^{\odot}$$
 (Fe³⁺, Fe²⁺) = +0.77V;

$$E^{\odot}$$
 (Fe²⁺, Fe) = -0.44V

$$E^{\odot}$$
 (Cu²⁺, Cu) = +0.34V;

$$E^{\odot}$$
 (Cu $^{\oplus}$, Cu) = +0.52V

$$E^{\odot} (Cu^{\oplus}, Cu) = +0.52V$$

 $E^{\odot} [O_2(g) + 4H^{\oplus} + 4e^{\odot} \longrightarrow 2H_2O] = +1.23V;$

$$E^{\odot} [O_2(g) + 4H^{\oplus} + 4e^{\odot} \longrightarrow 2H_2O] = +0.40V$$

$$E^{\odot} [O_2(g) + 2H_2O + 4e^{\odot} \longrightarrow 4OH^{\odot}] = +0.40V$$

$$E^{\odot}(Cr^{3+}, Cr) = -0.74V;$$

$$E^{\odot}(Cr^{2+}, Cr) = -0.91V$$

Match E of the redox pair in Column I with the values given in Column II and select the correct answer using the code given below the lists:

	Column I		Column II
P	$E^{\Theta}(Fe^{3+}, Fe)$	1.	-0.18 V
0	$E^{\Theta}(4H_2O \Longrightarrow 4H^{\oplus} + 4OH^{\Theta})$	2.	-0.4 V
	$E^{\Theta}(Cu^{2+} + Cu \longrightarrow 2Cu^{\oplus})$		- 0.04 V
	$E^{\Theta}(Cr^{3+}, Cr^{2+})$	4.	- 0.83 V

Codes:

	P	Q	R	S
(1)	4	1	2	3
(2)		3	4	1
(3)		2	3	4
(4)		4	1	2

(JEE Advanced 2013)

4. The metal that cannot obtained by electrolysis of an aqueous solution of its salts is:

- (2) Cr
- (4) Ca (3) Ag

(JEE Advanced 2014)

5. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_{∞} , respectively. The correct relationship between λ_C and λ_{∞} is given as: (where the constant B is positive)

(1)
$$\lambda_C = \lambda_\infty - (B) \sqrt{C}$$

$$(1) \lambda_{C} = \lambda_{\infty} - (B) \sqrt{C}$$

$$(2) \lambda_{C} = \lambda_{\infty} + (B) \sqrt{C}$$

$$(3) \lambda_{C} = \lambda_{\infty} + (B) C$$

$$(4) \lambda_{C} = \lambda_{\infty} - (B)C$$

(3)
$$\lambda_{\rm C} = \lambda_{\infty} + ({\rm B}) {\rm C}$$

$$(4) \lambda_{\rm C} = \lambda_{\infty} - ({\rm B}){\rm C}$$

(JEE Advanced 2014)

6. For the following electrochemical cell at 298 K, $Pt(s) | H_2(g, 1 \text{ bar}) H^+(aq. 1M) || M^{4+}(aq) | M^{2+}(aq) | Pt(s)$

$$E_{cell} = 0.092 \text{ V when } \frac{\left[M^{2+(aq)}\right]}{\left[M^{4+(aq)}\right]} = 10^x$$

Given:
$$E_{M^{4+}/M^{2+}}^0 = 0.151 \text{ V}; 2.303 \frac{RT}{F} = 0.059 \text{ V}$$

The value of x is

$$(1) -2$$

$$(2)-1$$

(JEE Advanced 2016)

7. For the following cell,

$$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$$

When the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+} , the expression for ΔG (in J mol⁻¹) is [F is Faraday constant; R is a gas constant; T is temperature; E^0 (cell) s

$$(2) 2.303 RT - 2.2 F$$

$$(3) 2.303 RT + 1.1 F$$

$$(4) -2.2 F$$

(JEE Advanced 2017)

Multiple Correct Answers Type

1. For the reduction of NO₃ ion in an aqueous solution, Fo is +0.96 V, the values of E^{\odot} for some metal ions are given below:

i.
$$V^{2+}(aq) + 2e^- \longrightarrow V;$$

$$E^{\odot} = -1.19 \text{ V}$$

ii.
$$Fe^{3+}(aq) + 3e^- \longrightarrow Fe$$
;

$$E^{\odot} = -0.04 \text{ V}$$

iii.
$$Au^{3+}(aq) + 3e^- \longrightarrow Au;$$

$$E^{\odot} = +1.40 \text{ V}$$

iv.
$$Hg^{2+}(aq) + 2e^{-} \longrightarrow Hg;$$

$$E^{\odot} = +0.86 \text{ V}$$

(IIT-JEE 2010)

The pair(s) of metals that is/are oxidized by NO₃ in aqueous solution is/are

- (1) Fe and Au
- (2) Hg and Fe
- (3) V and Hg
- (4) Fe and V

2. In a galvanic cell, the salt bridge

- (1) Does not participate chemically in the cell reaction
- (2) Stops the diffusion of ions from one electrode to another
- (3) Is necessary for the occurrence of the cell reaction
- (4) Ensures mixing of the two electrolytic solutions

(JEE Advanced 2014)

Linked Comprehension Type

Paragraph 1

The concentration of potassium ions inside a biological cell is at least 20 times higher than outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for a concentration cell involving a metal M is

$$M(s) \mid M^{\oplus}(aq; 0.05 \text{ molar}) \parallel M^{\oplus}(aq; 1 \text{ molar}) \mid M(s)$$

For the above electrolytic cell, the magnitude of the cell (HT-JEE 2010) potential is $|E_{cell}| = 70 \text{ mV}$.

1. For the above cell

(1)
$$E_{\text{cell}} < 0$$
; $\Delta G > 0$

(2)
$$E_{\text{cell}} > 0$$
; $\Delta G < 0$

(3)
$$E_{\text{cell}} < 0$$
; $\Delta G^{\odot} > 0$

(4)
$$E_{\text{cell}} > 0$$
; $\Delta G^{\odot} < 0$

2. If the 0.05 molar solution of M^{\oplus} is replaced by a 0.0025molar M[⊕] solution, then the magnitude of the cell potential would be

(3)
$$140 \text{ mV}$$
 (4) 700 mV

$$(4) 700 \text{ mV}$$

Paragraph 2

The electrochemical cell shown below is a concentration cell. $M \mid M^{2+}$ (saturated solution of sparingly soluble salt,

$$MX_2$$
) || M^{2+} (0.001 mol dm⁻³) | M

The emf of the cell depends on the difference in the concentration of M²⁺ ions at the of M²⁺ ions at the two electrodes. The emf of the cell at 298 is 0.059 V (IIT-JEE 2012) 0.059 V.

- 3. The solubility product (K_{sp} ; mol³ dm⁻⁹) of MX₂ at 298 based on the information available the given concentration cell is (Take 2.303 × R × 298/F=0.059 V)
 - (1) 1×10^{-15}
- (2) 4×10^{-15}
- (3) 1 × 10⁻¹²
- $(4) 4 \times 10^{-12}$
- 4. The value of ΔG (kJ mol⁻¹) for the given cell is (take 1F = 96500 C mol⁻¹)
 - (1) -5.7
- (2) 5.7
- (3) 11.4
- (4) 11.4

Matrix Match Type

1. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in Column I. The variation in conductivity of these reactions in Column II. Match Column I with Column II and select the correct answer using the code given below:

	Column I		Column II
P	$(C_2H_5)_3N + CH_3COOH$ X Y	1.	Conductivity decreases and then increases
Q	KI(0.1M) + AgNO ₃ (0.01M) X Y	2.	Conductivity decreases and then does not change much
R	CH ₃ COOH + KOH X Y	3.	Conductivity increases and then does not change much
S	NaOH + HI X Y	4.	Conductivity does not change much and then increases

Codes:			
P	Q	R	S
(1) 3	4	2	1
(2) 4	3	2	1
(3) 2	3	4	1
(4) 1	4	3	2
,			(JEE Advanced 2013)

Numerical Value Type

respectively).

1. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values, $pK_a(HX) - pK_a(HY)$, is (consider degree of ionization of both acids to be << 1)

(JEE Advanced, 2015)

2. All the energy released from the reaction $X \to Y$, $\Delta_r G^0 = -193 \text{ kJ mol}^{-1}$ is used for oxidizing M^+ as $M^+ \to M^{3+} + 2e^-$, $E^0 = -0.25 \text{ V}$.

Under standard conditions, the number of moles of M^+ oxidized when **one** mole of X is converted to Y is $[F = 96500 \text{ C mol}^{-1}]$ (JEE Advanced 2015)

3. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with a an area of cross section of 1 cm². The conductance of this solution was found to be 5 \times 10⁻⁷ S. The pH of the solution is 4. The value of limiting molar conductivity ($\Lambda^{\circ}_{\rm m}$) of this weak monobasic acid in aqueous solution is Z \times 10² S cm⁻¹ mol⁻¹. The value of Z is

(JEE Advanced 2017)

4. Consider an electrochemical cell: $A(s) | A^{n+} (aq, 2 M) | B^{2n+} (aq, 1 M) | B(s)$. The value of ΔH° for the cell reaction is twice that of ΔG° at 300 K. If the emf of the cell is zero, the ΔS° (in JK⁻¹ mol⁻¹) of the cell reaction per mole of *B* formed at 300 K is _____. (Give: $\ln(2) = 0.7$, R (universal gas constant) = 8.3 JK⁻¹ mol⁻¹. *H*, *S* and *G* are enthalpy, entropy and Gibbs energy,

(JEE Advanced 2018)

Answers Key

EXERCISES					46. (4)	47. (2)	48. (1)	49. (1)	50. (4)
Single Comm					51. (3)	52. (1)	53. (2)	54. (4)	55. (3)
	ct Answer T	ype			56. (2)	57. (3)	58. (3)	59. (3)	60. (2)
1. (3)	2. (1)	3. (2)	4. (1)	5. (1)	61. (3)	62. (1)	63. (4)	64. (3)	65. (1)
6. (4)	7. (4)	8. (1)	9. (4)	10. (2)	66. (3)	67. (3)	68. (2)	69. (2)	70. (3)
11.(1)	12. (4)	13. (2)	14. (4)	15. (1)	71. (4)	72. (1)	73. (1)	74. (3)	75. (3)
16. (2)	17. (4)	18. (4)	19. (2)	20. (4)	76. (1)	77. (1)	78. (1)	79. (4)	80. (3)
21.(1)	22. (2)	23. (1)	24. (2)	25. (3)	81. (2)	82. (1)	83. (1)	84. (4)	400
26. (4)	27. (1)	28. (2)	29. (2)	30. (3)	86. (1)	87. (1)	88. (2)	89. (1)	85. (1)
31. (3)	32. (2)	33. (4)	34. (4)	35. (2)	91. (2)	92. (4)	93. (1)		90. (4)
36. (2)	37. (2)	38. (4)	39. (3)	40. (4)	96. (3)	97. (1)		94. (3)	95. (2)
41. (4)	42. (3)	43. (1)	44. (3)	45. (3)			98. (3)	99. (1)	100. (3)
()	42. (3)	43. (1)	44. (3)	45. (5)	101. (3)	102. (4)	103. (3)	104. (3)	105. (1)

3.114 Phy	sical Chemistry									
106. (1)	107. (3)	108. (2)	109. (3)	110. (1)	46. (1, 3) 49. (1, 2,	2 1)	47. (1, 3) 50. (1, 3,		48. (1	1, 2)
111. (2)	112. (1)	113. (1)	114. (3)	115. (3)	52. (1, 3,		53. (1, 3,		54. (2	1, 3, 4)
116. (3)	117. (4)	118. (2)	119. (4)	120. (4)	55. (1, 2)	• /	56. (1, 2,		57. (1, 2, 4 ₎
121. (1)	122. (3)	123. (3)	124. (3)	125. (3)	58. (1, 2,	3, 4)	59. (1, 2,		60. ()	1, 2)
	122. (3) 127. (2)	128. (1)	129. (4)	130. (3)	61. (1, 3,	4)	62. (1, 2,		63. (1, 3)
126. (3)	132. (2)	133. (3)	134. (1)	135. (1)	64. (1, 3)		65. (1, 2,	(3, 4)		,
131. (1)	132. (2) 137. (3)	138. (3)	139. (2)	140. (2)	Linked Con	nprehensi	on Type			
136. (4)	137. (3) 142. (1)	143. (1)	144. (1)	145. (1)	1. (1)	2. (2)	3. ((3)	4. (2)	5. (1)
141. (3) 146. (2)	142. (1) 147. (1)	148. (1)	149. (4)	150. (1)	6. (4)	7. (3)	8. (` ^	9. (4)	10. (2)
151. (3)	152. (1)	153. (3)	154. (1)	155. (1)	11. (4)	12. (3)	13. (14. (3)	15. (2) 15. (4)
151. (3) 156. (4)	157. (1)	158. (4)	159. (2)	160. (2)	16. (1)	17. (2)	18. (19. (1)	13. (4)
161. (1)	162. (1)	163. (2)	164. (4)	165. (3)	10. (1)	177 (2)	200 ((-)	220 (1)	
166. (4)	167. (3)	168. (4)	169. (3)	170. (2)	Matrix Ma	tch Type				
171. (4)	172. (1)	173. (4)	174. (3)	175. (4)	0.37		T .			
176. (2)	177. (1)	178. (1)	179. (2)	180. (4)	Q.No.	a	b	С	d	e
181. (2)	182. (2)	183. (3)	184. (3,4)		1.	S	р	q	r	t
186. (1)	187. (4)	188. (1)	189. (2)	190. (2)	2.	q	r	p	t	S
191. (1)	192. (1)	193. (2)	194. (4)	195. (4)	3.	q	r	s	t	p
196. (2)	197. (1)	198. (3)	199. (1)	200. (1)	4.	r	р	t	q	S
201. (2,3)	202. (4)	203. (1)	204. (3)	205. (1)	5.			r	S	
206. (2)	207. (3)	208. (4)	209. (2)	210. (4)		р	q	-		_
211. (1)	212. (1)	213. (1)	214. (2)	215. (1)	6.	q, s	p, r	q, s	p, r	_
216. (3)	217. (4)	218. (1)	219. (4)	220. (2)	7. (1)	8. (2)	9. ((4)	10. (3)	
221. (1)	222. (4)	223. (2)	224. (1)	225. (1)					. ,	
226. (1)	227. (3)	228. (2)	229. (2)	230. (1)	Numerical	Value Typ	oe .			
231. (2)	232. (2)	233. (2)	234. (3)	235. (3)	1. (8)	2. (5)	3. ((6)	4. (10)	5. (3)
236. (3)	237. (2)	238. (2)	239. (4)	240. (4)	6. (3)	7. (5)	8. ((2)	9. (6)	10. (6)
241. (2)	242. (3)	243. (3)	244. (4)	245. (3)	11. (6)			,		
246. (3)	247. (3)	248. (1)	249. (1)	250. (4)	1					
251. (1)	252. (4)	253. (4)	254. (2)	255. (4)	ARCHIVES					
256. (3)	257. (2)	258. (1)	259. (3)	260. (4)	JEE Main					
261. (4)	262. (3)	263. (3)	264. (3)	265. (3)						
266. (4)	267. (2)				Single Corr	ect Answe	er Type			
					1. (3)	2. (3)	3. ((3)	4. (2)	5. (4)
lultiple Cor	rect Answers	S Type			6. (4)	7. (1)	8. (9. (4)	10. (2)
1. (1, 3)	2. ((1, 4)	3. (2, 3)	11. (1)	12. (2)	13. (• /	14. (1)	15. (2)
4. (1, 3)		(1, 4)	6. (1, 2				20. ((*)	1 · · (1)	
7. (2)		1, 2)			JEE Advanc	ed				
10. (4)	11. (9. (2, 3	•	Single Corr	ect Answe	er Type			
13. (1, 4)		•	12. (1, 2	Ť.	1. (4)			(4)	2 (4)	s (1)
[6. (1, 3)	7	1, 3, 4)	15. (1, 2			2. (4)	3. ((4)	4. (4)	5. (1)
10. (1, 3)	17. (1, 2, 3)	18. (1, 2	, 3, 4)	6. (4)	7. (2)				

19. (1, 2, 3)

22. (1, 3, 4)

25. (1, 3)

28. (3, 4)

31. (1, 2)

37. (2, 3)

40. (1, 3)

43. (2, 3)

34. (1, 2, 3)

20. (2, 3)

26. (1, 3)

29. (1, 2)

32. (1, 2)

35. (3, 4)

41. (1, 4)

38. (1, 3, 4)

44. (1, 2, 3)

23. (1, 2, 3, 4)

21. (3, 4)

24. (2, 3)

30. (1, 4)

33. (1, 2)

36. (3, 4)

45. (3)

39. (2, 3, 4)

42. (1, 2, 3)

27. (1, 2, 4)

Multiple Correct Answers Type

1. (2, 3, 4) **2.** (1, 2, 3)

Linked Comprehension Type

1. (2) **2.** (3) **3.** (2) **4.** (4)

Matrix Match Type

1. (1)

Numerical Value Type

4. $(-11.62 \text{ J mol}^{-1}\text{K}^{-1})$ 1. (3) **2.** (4) **3.** (6)

OVERVIEW

1. Limitations of thermodynamics

- a. Thermodynamics deals about the spontaneity of a reaction, i.e., the direction of the flow of heat, but does not discuss the rate of the reaction.
- b. It deals only with the initial and final state of the system but does not explain the path of the reaction, i.e., the mechanism of the reaction.
- c. It deals with the properties such as temperature, pressure, etc., of the matter in bulk (i.e., at macroscopic level) but does not tell anything about the individual atoms and molecules (i.e., at microscopic level).

So, the chapter of chemical kinetics is introduced to explain two of the above-mentioned limitations of thermodynamics.

- 2. The branch of chemistry that deals with the study of the speed or rate of chemical reactions, factors affecting the rates of reaction and the mechanism by which reactions proceed is known as chemical kinetics. The word "kinetics" is derived from the Greek word "kinesis" which means "movement."
- 3. Rate of reaction: It is the change in the concentration of any one of the reactants or products per unit time.

The rate of reaction in terms of reactant (R) or product (P) is written as:

Rate of reaction =
$$\frac{-\Delta[R]}{\Delta t}$$
 = $+\frac{\Delta[P]}{\Delta t}$

where Δ [R] = R₂ - R₁ and Δ P = P₂ - P₁ and Δ t = t₂ - t₁

a. Significance of negative and positive sign: Rate of reaction is always positive. Negative sign along with first term signifies a decrease in the concentration of the reactant and positive sign along with the second term indicates an increase in the concentration of the product.

Note: Negative sign along with first term is not used in calculation part.

- **b.** Units of rate of reactions: In aqueous reactions, the unit of rate is mol L^{-1} t^{-1} or M t^{-1} whereas in the case of gaseous reaction the unit of rate is atm t^{-1} .
- c. Average rate and instantaneous rate of reaction
 - i. According to the law of mass action, the rate of reaction depends upon the molar concentrations of the reactants which decreases with time while those of products increases with time. Therefore, the rate of reaction does not remain constant throughout.

Thus, the rate of reaction as defined above is the average rate of reaction during the time interval taken.

Thus, average rate of reaction (r_{av})

$$= \frac{-\Delta[R]}{\Delta t} = + \frac{\Delta[P]}{\Delta t}$$
or $r_{av} = \frac{\Delta x}{\Delta t}$

- ii. The instantaneous rate of reaction, i.e., the rate of reaction at any instant of time is the change of concentration per unit time of any one of the reactants or products at that particular time.
- $\therefore \text{ Instantaneous rate } (r_{\text{inst}}) = \frac{dx}{dt}$

For example, for the reaction, $R \longrightarrow P$

$$r_{\text{inst}} = \frac{-d[R]}{dt} = +\frac{d[P]}{dt}$$

Actually,
$$r_{\text{inst}} = -\frac{\Delta[R]}{\Delta t}$$
 or $+\frac{\Delta[P]}{\Delta t}$
 $\Delta t \longrightarrow 0 \Delta t \longrightarrow 0$

Note: Symbol Δ is used for large change, i.e., for average rate whereas symbol "d" is used for small change, i.e., for instantaneous rate.

d. Expressing the rate of reaction in terms of different reactants and products

For the general reaction:

$$aA + bB \longrightarrow cC + dD$$

Rate =
$$\frac{1}{a} \left(\frac{-d[A]}{dt} \right) = \frac{1}{b} \left(\frac{-d[B]}{dt} \right) = \frac{1}{c} \frac{d[C]}{dt}$$

$$= \frac{1}{d} \frac{d[D]}{dt}$$

Note: In aqueous solution, the rate of reaction is not expressed in terms of change of concentration of water because there is a negligible change, e.g., from 55.5 M to 55.49 M.

e. Rate constant: It is equal to the rate of reaction when the concentration of each reaction is unity, i.e., 1 mol L⁻¹. It is a constant for a particular reaction at a given temperature and also known as specific rate constant or specific reaction rate.

For a general reaction:

$$aA + bB \longrightarrow Products$$

Rate =
$$\frac{dx}{dt} = k[A]^a [B]^b$$
; if $[A] = [B] = 1 M$
Then = $\frac{dx}{dt} = k$

- f. Units of rate constant for the nth order reaction $k = (\text{mol } L^{-1})^{1-n} t^{-1} \text{ or } (M)^{1-n} t^{-1}.$
- g. Relation between rate of reaction in atm t^{-1} and mol $L^{-1}t^{-1}$

$$PV = nRT$$

$$\frac{\Delta(n/V)}{\Delta t} \text{ mol } L^{-1} t^{-1} = \frac{\Delta P}{\Delta t} \times \frac{1}{RT}$$

4. Relation between the rate of formation/decomposition of any one of the reactant/product given in mass t^{-1} and the rate of formation/decomposition of another reactant/product is required in mass t^{-1} .

For general formula,

$$aA + bB \longrightarrow cC + dD$$

$$\frac{-d[A]}{a dt} = \frac{-d[B]}{b dt} = \frac{d[C]}{c dt} = \frac{d[D]}{d dt}$$

For example:

$$\therefore \frac{-d[A]}{dt} = \frac{a}{c} \frac{d[C]}{dt} \text{ moles } L^{-1} t^{-1}$$

a.
$$\frac{-d[A]}{dt} \text{ in mass } t^{-1} = \frac{a}{c} \frac{d[C]}{dt} \times \frac{Mw \text{ of } A}{Mw \text{ of } C} \text{ mass } t^{-1}$$

b.
$$\frac{-d[A]}{dt} \text{ in mass } t^{-1} = \frac{a}{d} \frac{d[D]}{dt} \times \frac{Mw \text{ of } A}{Mw \text{ of } D} \text{ mass } t^{-1}$$
Similarly

c.
$$\frac{-d[B]}{dt} \text{ in mass } t^{-1} = \frac{b}{c} \frac{d[C]}{dt} \times \frac{Mw \text{ of } B}{Mw \text{ of } C} \text{ mass } t^{-1}$$

d.
$$\frac{-d[B]}{dt}$$
 in mass $t^{-1} = \frac{b}{d} \frac{d[D]}{dt} \times \frac{Mw \text{ of } B}{Mw \text{ of } D} \text{ mass } t^{-1}$

5. Order of reaction: The sum of exponents (power) to which the concentration terms in the rate law equation are raised to express the observed rate of the reaction determined experimentally is called the order of reaction.

For rate law,

Rate =
$$k[A]^a[B]^b[C]^c$$

$$Order = a + b + c$$

- 6. Reactions of various orders: In such reactions, the concentration of various reactants except one remain practically constant during the course of reaction.
- a. Zero order reaction: A reaction in which the rate is independent of the concentration of the reactant molecules. i.e., the rate is proportional to the zeroth power of the concentration of reactants.

$$-\frac{dx}{dt} = k[A]^0 = k$$

i.e., the reaction velocity remains constant throughout the progress of the reaction. The concentration decreases linearly with time.

$$[A]_t = [A]_0 - kt$$

$$t_{\text{completion}} = \frac{[A]_0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

The units of k are mol L⁻¹ time⁻¹.

Half-life time,
$$t_{1/2} = \frac{[A]_0}{2k}$$

b. First order reaction: The rate depends upon the concentration of one reactant only.

$$\frac{-dx}{dt} = k[A]$$

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

where t = time, a = initial concentration, and (a-x) = concentration at time t.

A change in concentration unit does not affect the numerical value of k. Thus, for first order reactions, any quantity which is proportional to concentration can be used in the place of concentration in the integrated equation.

The time taken for the completion of same fraction of change is independent of initial concentration. When x = 0.5a and $t = t_{1/2}$

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log 2 = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{k}$$

Thus, $t_{1/2}$ is independent of initial concentration.

The equation of the first order can also be written in the following form when initial concentration is not known.

$$k = \frac{2.303}{(t_2 - t_1)} \log \frac{(a - x_1)}{(a - x_2)} = \frac{2.303}{(t_2 - t_1)} \log \frac{[A]_{t_1}}{[A]_{t_2}}$$

The unit of k is time⁻¹.

i. Average life (λ) = $\frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.44t_{1/2}$

The time in which 63.2% substance undergoes decay is called average life.

ii. Relation between $t_{1/2}$ and $t_{x\%}$ (amount decomposed):

$$t_{x\%(\text{decomposed})} = \frac{2.3}{k} \log \left(\frac{100}{100 - x} \right) \qquad \dots (i)$$

$$t_{1/2} = \frac{0.69}{k} = \frac{0.3 \times 2.3}{k}$$
 ...(ii)

Dividing Eq. (ii) by (i), we get

$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log\left(\frac{100}{100 - x}\right)}$$

iii. Relation between $t_{x\%}$ and $t_{y\%}$ (amount decomposed):

$$\frac{t_{x\%}}{t_{y\%}} = \frac{\log\left(\frac{100}{100 - x}\right)}{\log\left(\frac{100}{100 - y}\right)}$$

where x% and y% are the percentages of substance decomposed.

iv. Relation between $t_{1/2}$ and $t_{r\%}$ (amount left).

$$\frac{t_{1/2}}{t_{x\%(\text{left})}} = \frac{0.3}{\log\left(\frac{100}{x}\right)}$$

v. Relation between $t_{x\%}$ and $t_{y\%}$ (amount left):

$$\left(\frac{t_{x\%}}{t_{y\%}}\right)_{\text{left}} = \frac{\log\left(\frac{100}{x}\right)}{\log\left(\frac{100}{y}\right)}$$

vi. $t_{1/2} = \frac{0.693}{L}$ for first order reaction

and
$$t_{3/4}=2t_{1/2}$$
 or $t_{75\%}=2t_{1/2},\,t_{87.5\%}=3t_{1/2}$ and similarly $t_{99.9\%}=10t_{1/2}$ and $t_{25\%}=0.4t_{1/2}$ $t_{96.87\%}=5t_{1/2},\,t_{93.75\%}=2t_{75\%}=4t_{1/2}$ since $t_{75\%}=2t_{1/2}$ In general, for the n th order reaction,

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

vii. Amount of substance left after n half lives:

$$A_0 \left(\frac{1}{2}\right)^n$$
 or $\frac{A_0}{2^n}$ and $n = \frac{\text{Total time}}{t_{1/2}}$

viii. For nth fraction of the reaction to complete, time taken:

$$t_{1/n} = \frac{2.303}{k} \log \frac{1}{\left(1 - \frac{1}{n}\right)}$$

ix. Starting with two different concentrations a_1 and a_2 for the same reaction, the half lives $(t_{1/2})_1$ and $(t_{1/2})_2$ are determined.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$
Slope = $\frac{-k}{2.303}$
or $n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log(t_{1/2})_1}$

or $n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}$

n is the order of reaction.

c. Second order reactions: Reaction rate depends upon the concentration of two reactants.

$$\frac{dx}{dt} = k[A][B] = k[A]^2$$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

[(a-x)] and (b-x) are the concentration of A and B after time interval t.]

When concentrations of both the reactants are same,

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

(x is the concentration changed in time interval t)

Half-life period, $t_{1/2} = 1/ka$, i.e., inversely proportional to initial concentration. The units of k are litre mol⁻¹ time⁻¹.

d. Third order reaction: Expression for a third order reaction of the type

$$3A \rightarrow products$$

$$\frac{dx}{dt} = k[A]^3$$

$$k = \frac{1}{t} \frac{x(2a-x)}{2a^2(a-x)^2}$$

The units of k are L^2 mol⁻² time⁻¹.

7. In general for *n*th order $(n \ge 2)$

 $nA \longrightarrow Products$

$$k_n = \frac{1}{(n-1)t} \left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$
and $t_{1/2} = \frac{2^{n-1} - 1}{k_n (n-1) [A]_0^{n-1}}$ $(n \ge 2)$

- 8. Refer to Table 4.1 for units of rate constant.
- 9. Refer to Table 4.3 for expressions for rate constant for reactions of different orders.
- 10. Refer to Table 4.4 for order of reaction and $t_{1/2}$ values along with the units of rate constant.
- 11. Refer to Table 4.2 for difference between molecularity and order of a reaction.

12. Elementary or simple reactions: The reactions taking place in one step are called elementary reactions. For an elementary reaction, the order of reaction should be equal to molecularities and further molecularites should be integral.

For example, the rate law for the reaction:

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

is
$$\frac{d[HBr]}{dt} = k[H_2][Br_2]^{\frac{1}{2}}$$
.

If the reaction were elementary, the reaction rate would involve one molecule of H2 reacting with one molecule of Br₂ to give the bimolecular rate law.

$$\frac{d[HBr]}{dt} = k[H_2][Br_2]$$

Since this is not the observed rate law, the reaction is not elementary.

13. Complex reactions: The reactions which do not take place in one step are called complex reactions. The reactions in which all the atoms, ions, or molecules as represented in the balanced chemical reaction may not come together to collide simultaneously. For example,

$$5\mathrm{Br}^{\ominus}(\mathrm{aq}) + \mathrm{BrO}_3^{\ominus}(\mathrm{aq}) + 6\mathrm{H}^{\oplus}(\mathrm{aq}) \longrightarrow 3\mathrm{Br}_2(\mathrm{aq}) + 3\mathrm{H}_2\mathrm{O}(\mathrm{l})$$
 It is impossible for all the 12 ions of the reactant to come together simultaneously to collide. Such reactions are called *complex reactions*. Such reactions take place in a sequence of a number of steps. Each of these step reactions is called an elementary reaction. Molecularity is defined only for an elementary reaction not for the complex reactions.

Note: Different steps of complex reaction are also elementary reactions.

- 14. Rate-determining step: The different elementary reactions of a complex reaction do not take place at the same rate. The overall rate of the reaction depends upon the slowest step. Hence, the slowest step is called the rate-determining step.
- 15. Mechanism of the reaction: A series of step reactions or elementary reactions proposed to account for the overall reaction is called the mechanism of the reaction.
- 16. Reactions for which steady state hypothesis is valid: A reaction may take place in a number of steps and may have several intermediates. In the steady state hypothesis, we assume that the intermediates are so reactive that after a brief initial period (called induction period) their concentrations rise from zero to a small value and remain constant for most of the duration of the reaction, i.e., we can assume that change in the concentration with time for these reactive intermediates is zero. This assumption is very helpful for deriving the rate expression for complex reactions.

Note: Negative, zero, and fractional orders are obtained whenever the desired reaction does not occur in single elementary step.

17. a. Rate law for opposed or reversible elementary reactions

$$\mathbf{i.} \quad \mathbf{H}_2 + \mathbf{I}_2 \xrightarrow{k_1 \atop k_2} 2\mathbf{H}\mathbf{I}$$

Rate =
$$\frac{1}{2} \frac{d[HI]}{dt} = k_1[H_2][I_2] - k_2[HI]^2$$

ii.
$$2NO_2 \stackrel{k_1}{\longleftarrow} N_2O_4$$

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 - k_2[N_2O_4]$$

Case I: First order-opposed by first order

$$A \stackrel{k_1}{\longleftarrow} B$$

$$\begin{bmatrix} t = 0 \\ t = t \end{bmatrix} \qquad \begin{array}{c} a & 0 \\ a - x & x \end{array}$$

$$t = \frac{2.303}{(k_1 + k_2)} \log \frac{X_{eq}}{X_{eq} - x}$$

 $(X_{eq} = [B]$ formed at equilibrium)

Case II: First order-opposed by first order

$$A \stackrel{k_1}{\rightleftharpoons} B.$$

$$\begin{bmatrix} t = 0 \\ t = t \end{bmatrix} \qquad \begin{array}{c} a & b \\ a - x & b + x \end{array}$$

$$t = \frac{2.303}{(k_1 + k_2)} \log \frac{X_{eq}}{X_{eq} - x}$$

 $(X_{eq} = [B]$ formed a equilibrium)

b. Rate law for side or parallel or concurrent elementary reactions

A single reactant gives two products B and C simultaneously with different decay constants. For first order reaction:

A
$$\xrightarrow{k_1}$$
 B (90%) (Main reaction)
 $\xrightarrow{k_2}$ C (10%) (Side reaction)

Rate =
$$-\frac{d[A]}{dt}$$
 = $k_1[A] + k_2[A] = (k_1 + k_2)[A]$
= $k_{av}[A]$

If after a time interval say x M of B are formed and y M of C are formed, then if reaction is carried out with A, when t = 0, [B] = [C] = 0.

$$\therefore \frac{x}{y} = \frac{k_1}{k_2}$$

Also
$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$

$$k_1 = (\% \text{ yield of B}) \times k_{av}$$

$$\Rightarrow$$
 % yield of B = $\frac{k_1}{k_{av}} = \frac{k_1}{k_1 + k_2}$

$$k_2 = (\% \text{ yield of C}) \times k_{av}$$

$$\Rightarrow$$
 % yield of C = $\frac{k_2}{k_{av}} = \frac{k_2}{k_1 + k_2}$

Some examples:

i. Phenol $\xrightarrow{\text{Nitraion}} o$ -nitrophenol + p-nitrophenol

ii.
$$C_2H_5Br + KOH$$
 $H_2C = CH_2 + KBr + H_2O$ $C_2H_5OH + KBr$

c. Rate law for consecutive or sequential reactions:
A reactant (A) decomposes to (B), which in turn decomposes to (C), i.e.,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\therefore \frac{-d[\mathbf{A}]}{dt} = k_1[\mathbf{A}], \qquad \frac{-d[\mathbf{B}]}{dt} = k_1[\mathbf{A}] - k_2[\mathbf{B}],$$

$$\frac{-d[\mathbf{C}]}{dt} = k_2[\mathbf{B}]$$

If t = 0, [B] = 0, and $k_1 < k_2$, then at t = t.

$$[B]_{t} = \frac{k_{1}[A]_{0}}{k_{2} - k_{1}} \left[e^{-k_{1}t} - e^{-k_{2}t} \right]$$

(where $[A]_0$ = Initial concentration of A)

Also maximum concentration of [B] at time t is given by

$$t_{\text{max}} = \frac{2.303}{k_2 - k_1} \log \left[\frac{k_2}{k_1} \right]$$

- d. Refer to Table 4.6(a) for graphs.
- 18. Pseudo unimolecular (or pseudo first order) reactions:

The reactions having molecularity ≥ 2 but order of reaction 1 are called pseudo first order reactions.

Examples: (i) inversion of cane sugar, (ii) hydrolysis of ester in acidic medium.

Units of the rate constant (k') of a pseudo unimolecular reaction

$$k'$$
 (for pseudo first order) = $\frac{k \text{ (for first order)}}{[\text{H}_2\text{O}]}$
= $\frac{t^{-1}}{\text{mol K}^{-1}} = \text{L mol}^{-1} t^{-1}$

Unis of k' represent a second order reaction.

19. Pseudo bimolecular (or pseudo second order) reactions: The reactions in which molecularity ≥ 3 but the order of reaction = 2. Examples: Hydrolysis of ester in basic medium

(or saponification of ester).

Units of the rate constant (k') of a pseudo bimolecular reaction

$$k'$$
 (for pseudo second order) = $\frac{k(\text{for second order})}{[\text{H}_2\text{O}]}$
= $\frac{\text{mol}^{-1} \text{L}^1 t^{-1}}{\text{mol} \text{L}^{-1}}$

 $\therefore k' = \text{mol}^{-2} L^2 t^{-1}$ (Units of k' represent a third order reaction)

20. Typical first order gas phase reactions

$$k = \frac{2.303}{t} \log \frac{p_0}{(2p_0 - p_t)}$$

where p_0 = initial pressure and $p_{\rm t}$ = total pressure after decomposition.

21. Threshold and activation energy of reactions: The minimum energy which the colliding molecules must have in order that the collision between them may be effective is called *threshold energy*.

The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold energy is called *activation energy*.

In other words, difference between the threshold energy and the average kinetic energy of the reactant molecules i.e.,

Activation energy (E_a)

= Threshold energy (E_t) – (Average kinetic energy of the reactants)

or

Threshold energy (E_t)

= E_a + Energy possessed by reactants (i.e., potential energy of reactants)

or $= E_a + PE$ of reactants

- **a.** For endothermic reactions $[E_a(f) < E_a(b)]$:
- **b.** For exothermic reactions $[E_a(f) < E_a(b)]$:

22. Effect of catalyst on the rate of reaction:

The presence of catalyst lowers the potential energy barrier and the reaction follows a new alternate path which requires less E_a and reaction becomes faster because more reactant molecules can cross the energy barrier and change into products as shown in Figures 4.20 to 4.22.

Some of the characteristics of a catalyst are as follows:

- a. A catalyst cannot initiate a reaction. It can only accelerate the rate of reaction and does not catalyze nonspontaneous reaction.
- **b.** A small amount of catalyst can bring about a large change in the rate of reaction.
- c. A catalyst neither alter free energy change (ΔG) nor enthalpy change (ΔH) of the reaction.
- **d.** For a reversible reaction, it increases the speed of forward and backward reactions to the same extent. Hence, it does not change the equilibrium constant of the reaction (i.e., k_{eq} or k_{e} or k_{p}). It simply helps to attain the equilibrium faster.
- 23. Kinetic stability of fuels: The combustion of fuels such as coal in the presence of air or O_2 is thermodynamically feasible $(C + O_2 \rightarrow CO_2)$ because $\Delta G = -\text{ve}$. Yet fuels are quite stable even in the presence of air or O_2 , because of high E_a of the reaction. On heating, the fuel and air absorb heat which provides necessary E_a and hence combustion continues. Thus, fuels which are thermodynamically unstable are kinetically stable.

The stability of fuels is due to the existence of *energy* barriers between the reactants and the products. The

existence of life on earth is due to these energy barriers, otherwise all the fuel on the earth would have burnt away by themselves.

24. Effect of temperature on rate constant

a. Temperature has a marked effect on the rate of reaction. For most of the reactions, the rate of reaction becomes nearly double or even more for 10° rise of temperature. The effect of temperature is usually expressed in terms of temperature coefficient which is defined by the equation

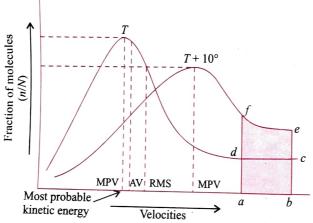
Temperature coefficient (n)

$$= \frac{\text{Rate constant at } T + 10^{\circ} (308 \text{ K})}{\text{Rate constant at } T (298 \text{ K})}$$

For most of the reactions, 2 < n < 3.

$$\frac{Z_{308}}{Z_{298}} = \sqrt{\frac{308}{298}} = 1.016 \quad Z \propto \sqrt{T}$$

b. If a fraction of molecules is plotted versus corresponding kinetic energies (called Maxwell's distribution curve of energies), the following graph is obtained (Refer to Fig. 4.14 also).



MPV : AV : RMS = 1 : 1.128 : 1.224

$$= \sqrt{\frac{2RT}{Mw}} : \sqrt{\frac{8RT}{\pi Mw}} : \sqrt{\frac{3RT}{Mw}}$$

The graph explains an increase in the rate of reaction, with increase in temperature mainly due to increase in the number of effective collisions. The graph shows that with the increase of temperature, peak shifts forward but also downward, which means that with increase of temperature,

- i. The most probable kinetic energy increases, and
- ii. The fraction of molecules possessing most probable kinetic energy decreases.

25. Arrhenius equations

- a. Quantitatively, the effect of temperature on the rate of equation and hence rate constant (k) was shown by Arrhenius and this equation is called *Arrhenius equation*.
- **b.** Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$

or
$$\log k = \log A - \frac{E_a}{2.303RT}$$
 where

k = Rate constant

A = Frequency factor for binary collisions or pre-

 $E_a = Activation energy$

 $R = \text{Gas constant} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

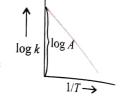
For two different temperatures T_1 and T_2 ,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where k_1 and k_2 are rate constants at temperatures T_1 and T_2 , respectively.

Plot of $\log k$ versus 1/T

Intercept =
$$\log A$$
;
Slope = $-\frac{E_a}{2.303R}$



- c. The two quantities A and E_a are collectively called *Arrhenius* parameters.
- **d.** The factor $e^{-E_a/RT}$ in the Arrhenius equation is called *Boltzmann factor*.
- e. The pre-exponential factor (A) is dimensionless and has the same unit as that of rate constant for first order reaction, i.e., Time⁻¹ (e.g., min⁻¹ or s⁻¹, etc.). That is why A is called *frequency factor*.
- f. The temperature dependence of k can be found by taking the derivative of Arrhenius equation w.r.t. T, giving

$$k = Ae^{-E_{a}/RT}$$

$$\frac{dk}{dT} = Ae^{-E_{a}/RT} \cdot \frac{E_{a}}{RT^{2}}$$

$$= k \cdot \frac{E_{a}}{RT^{2}}$$

The positive value of E_a , the temperature dependence will be greater for reaction with large value of E_a .

- g. Only reactions whose E_a falls in the range of 50-55 kJ mol⁻¹ or 12-13 kcal mol⁻¹ are found to double their rate for this range (i.e., from 298 to 308 K) of temperature.
- **h.** The fraction of molecules having energy equal to or greater than activation energy (E_a) is given by the expression:

$$x = \frac{n}{N} = e^{-E_{a}/RT}$$

or
$$\log x = -\frac{E_a}{2.303RT}$$

- i. Arrhenius constant $(A) = PZ_{AB}$ where P is the orientation or probability or steric factor and Z_{AB} represents collision frequency of reactants A and B.
- j. The E_a of a reaction cannot be zero. According to the Arrhenius equation, $k = Ae^{-Ea/RT} = Ae^{\circ} = A$, i.e., k = A. It means every collision results into a chemical reaction which is not true

the Afficiate of
$$k = Ae^{E_a/RT} = Ae^x$$
 (where $x = E_a/RT$)

If x << 1, we have

$$e^{x} = 1 + x + \frac{x^{2}}{2!} + \frac{x^{3}}{3!} + \dots = 1 + x$$

(neglecting higher power of x)

$$=1+E_a/RT$$

 $\therefore k = A(1 + E_a/RT)$, i.e., k >> A, which is impossible.

1. Rate constant when the temperature is very high (i.e., $T = \infty$) is not feasible.

At
$$T = \infty$$
, $k = Ae^{-E_a/RT} = Ae^{\circ} = A$

Rate constant = Collision frequency which is not feasible as explained in point (j) above.

m. Rate constant (k) cannot be greater than or equal to A, but it can be less than A.

4.1 INTRODUCTION

The feasibility of a reaction can be predicted with the help of thermodynamic principles. Besides this, relative amounts of reactants and products at equilibrium position of the reaction can also be predicted. However, the thermodynamic principles do not provide any information regarding the speed of a given reaction, i.e., how much time a given feasible reaction will take for its completion. It is also not possible to predict how the speed of a given reaction gets affected by changing the concentration of various reactants and products or by changing the experimental conditions. The study of reaction rates and their mechanisms, is called *chemical kinetics*. The word kinetics is derived from the Greek word *kinesis* meaning movement.

4.2 RATE OF A CHEMICAL REACTION

The progress of a chemical reaction is monitored by measuring the concentration(s) of reactants and/or products as a function of time. Here we assume that the volume of the system remains constant and there is no removal from or addition to the reaction vessel of any of the reactants or products. Under such conditions, we find that during the course of a reaction the concentration of reactants decreases while that of products increases.

Consider a hypothetical reaction: $R \longrightarrow P$, in which one mole of the reactant R produces one mole of the product P. The rate of reaction may be expressed in either of the following two ways:

a. The rate of disappearance or decrease in the concentration of R (reactants):

Rate of reaction =
$$\frac{\text{Decrease in the concentration of R}}{\text{Time taken}}$$

b. The rate of increase in the concentration of P (products):

Rate of reaction =
$$\frac{\text{Increase in the concentration of P}}{\text{Time taken}}$$

If $[R]_1$ and $[P]_1$ are concentrations of R and P, respectively, at time t_1 and $[R]_2$ and $[P]_2$ are concentrations at time t_2 , then

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta[P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R

$$= \frac{\text{Decrease in the concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \qquad ...(i)$$

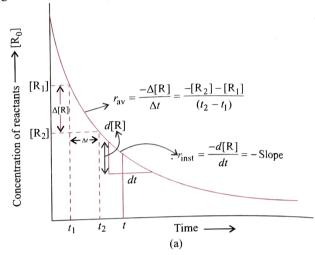
Rate of appearance of P

=
$$\frac{\text{Increase in the concentration of P}}{\text{Time taken}} = + \frac{\Delta[P]}{\Delta t}$$
 ... (ii)

Since, $\Delta[R]$ is a negative quantity (as the concentration of reactants is decreasing), it is multiplied with -1 to make the rate of reaction a positive quantity.

Equations (i) and (ii) given above represent the average rate of reaction, r_{av} .

The average rate depends upon change in the concentration of reactants or products and the time taken for that change to occur (Fig. 4.1).



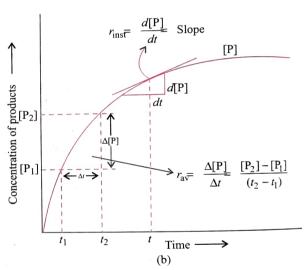


Fig. 4.1 Instantaneous and average rate of reaction

For a chemical reaction, the average rate depends on the value of t_2 and t_1 chosen. Initially, the rate is very fast and later on the rate decreases. Like instantaneous speed, the instantaneous rate also changes and the instantaneous rate has to be at a particular instant (time t). Mathematically, we represent instantaneous rate by

$$-\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \text{ or } r_{\text{inst}} = \frac{-d[R]}{dt} = \frac{d[P]}{dt} \qquad \dots \text{(iii)}$$
as $\Delta t \to 0$.

It may be noted from Eqs. (i) and (ii) that the instantaneous rate can be determined by drawing a tangent at time t on either of the curves for concentration versus time t of R and P. The slope of the curve at time t is related to the instantaneous rate by the equation:

$$r_{\text{inst}} = -\text{Slope (for R)} = -d [R]/dt \text{ or}$$

= Slope (for P) = $d[P]/dt$

Units of the rate of a reaction

From Eqs. (i) and (ii), it is clear that the unit of rate is concentration $time^{-1}$. For example, if the concentration is in mol L^{-1} and the time is in seconds then the unit will be mol L^{-1} s⁻¹. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the unit of the rate equation will be atm s⁻¹.

Expression of rate

Consider the following reaction between CO and NO₂:

$$CO + NO_2 \longrightarrow CO_2 + NO$$

The above equation shows that when one mole of CO reacts with one mole of NO₂, one mole each of CO₂ and NO are formed. The average rate of reaction can be expressed either by decrease in the concentration of any one of the reactants (CO or NO₂) or by increase in the concentration of any one of the products (CO, or NO).

Thus,
$$-\frac{\Delta [CO]}{\Delta t} = -\frac{\Delta [NO_2]}{\Delta t} = \frac{\Delta [CO_2]}{\Delta t} = \frac{\Delta [NO]}{\Delta t}$$

However, for the reaction,

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

it is observed that when 2 moles of H_2O_2 decompose, one mole of O_2 is formed in the same time interval. The rate of increase in the concentration of O_2 , therefore, is half that of the disappearance of the concentration of H_2O_2 in the same time interval.

So,
$$\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[H_2O_2]}{\Delta t}$$

In general, for a reaction,

$$n_1 A + n_2 B \longrightarrow m_1 C + m_2 D$$

The rate expression may be expressed as

$$-\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2}\frac{\Delta[B]}{\Delta t} = \frac{1}{m_1}\frac{\Delta[C]}{\Delta t} = \frac{1}{m_2}\frac{\Delta[D]}{\Delta t}$$

Thus, for the reaction,

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

stoichiometric coefficients of NO, O_2 , and NO_2 are 2, 1, and 2, respectively, and hence the rate is given by

Rate =
$$\frac{-d[NO]}{2dt} = \frac{-d[O_2]}{dt} = \frac{-d[NO_2]}{2dt}$$

Similarly, for the reaction

$$5Br^{\odot}(aq) + BrO_3^{\odot}(aq) + 6H^{\oplus}(aq) \longrightarrow 3Br_2(aq) + 3H_2O(1)$$

Rate =
$$\frac{-d[Br^{\oplus}]}{5dt} = \frac{-d[BrO_3^{\ominus}]}{dt}$$

= $\frac{-d[H^{\oplus}]}{6dt} = \frac{d[Br_2]}{3dt}$

In aqueous solution, the change in the concentration of water is very small and hence we do not use change in the concentration of water for expressing the rate.

For a gaseous reaction at constant T, the concentration is directly proportional to the partial pressure of a species and hence the rate can also be expressed as the rate of change in the partial pressure of the reactant or product.

For a general reaction,

$$aA + bB = cC + dD$$

the rate of the reaction is defined as:

Rate of reaction =
$$\frac{1}{a} \frac{-d[A]}{dt} = \frac{1}{b} \frac{-d[B]}{dt}$$

= $\frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$

Let us write instantaneous rate expressions for some reactions:

a.
$$H_2 + I_2 \rightleftharpoons 2HI$$

Rate of reaction =
$$\frac{-d[H_2]}{dt} = \frac{-d[I_2]}{dt} = \frac{1}{2} \frac{d[HI]}{dt}$$

b.
$$2N_2O_5 \Longrightarrow 4NO_2 + O_2$$

Rate of reaction =
$$\frac{1}{2} \frac{-d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

c.
$$N_2 + 3H_2 \Longrightarrow 2NH_3$$

Rate of reaction =
$$\frac{-d[N_2]}{dt} = \frac{1}{3} \frac{-d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

ILLUSTRATION 4.1

The decomposition of N_2O_5 in CCl_4 solution at 318 K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially, the concentration of N_2O_5 is 2.33 M and after 184 min, it is reduced to 2.08 M. The reaction takes place according to the equation:

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Calculate the average rate of this reaction in terms of hours, minutes, and seconds. What is the rate of production of NO₂ during this period?

Sol. Rate of reaction

$$= -\frac{\Delta [N_2O_5]}{\Delta t}$$

$$= -\frac{(2.33 - 2.08) \text{ mol } L^{-1}}{184 \text{ min}}$$

Note: -ve sign is not included in calculation.

$$= 1.36 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

If time =
$$184 \text{ min} = 3.067 \text{ hr}$$

Rate =
$$-\frac{(2.33 - 2.08) \text{ mol } L^{-1}}{3.067 \text{ hr}}$$

$$= 8.16 \times 10^{-2} \text{ mol L}^{-1} \text{ hr}^{-1}$$

If time =
$$184 \times 60 = 11040 \text{ s}$$

Rate =
$$-\frac{(2.33 - 2.08) \text{ mol } L^{-1}}{11040 \text{ s}}$$

$$= 2.26 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate =
$$-\frac{\Delta [N_2O_5]}{2\Delta t} = \frac{\Delta [NO_2]}{4\Delta t}$$

$$\therefore \frac{\Delta (NO_2)}{\Delta t} = -\frac{4}{2} \frac{[N_2O_5]}{\Delta t} = 2 \times \frac{-[N_2O_5]}{\Delta t}$$
= 2 × 1.36 × 10⁻³ mol. L⁻¹ min⁻¹
= 2.72 × 10⁻³ mol. L⁻¹ min⁻¹

Express the rate of the following reactions:

a.
$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

b.
$$2NO_2 \longrightarrow 2NO + O_2$$

in terms of the concentrations of reactants and products.

Sol.

a. For the reaction, $PCl_5 \longrightarrow PCl_3 + Cl_2$

Rate of reaction =
$$\frac{-d [PCl_5]}{dt} = \frac{d [PCl_3]}{dt} = \frac{d [Cl_2]}{dt}$$

b. For the reaction,

$$2NO_2 \longrightarrow 2NO + O_2$$

Rate of reaction =
$$\frac{1}{2} \frac{-d [\text{NO}_2]}{dt} = \frac{1}{2} \frac{d [\text{NO}]}{dt} = \frac{d [\text{O}_2]}{dt}$$

ILLUSTRATION 4.3

For each of the following reactions, express the given rate of change of concentration of the reactant or product in terms of the rate of change of concentration of other reactants or products in that reaction:

a.
$$H_2O_2 + 2H^{\oplus} + 3I^{\odot} \longrightarrow I_3^{\odot} + 2H_2O;$$

$$\frac{-d\left[\mathbf{I}^{\odot}\right]}{dt} = ?; \quad \frac{-d\left[\mathbf{H}^{\oplus}\right]}{dt} = ?$$

b.
$$16H^{\oplus} + 2MnO_4^{\ominus} + 10I^{\ominus} \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2;$$

$$\frac{-d \left[\mathrm{MnO_4}^{\odot}\right]}{dt} = ?$$

c.
$$4NH_3 + 5O_2 \longrightarrow 4NO_2 + 6H_2O;$$
 $\frac{-d[NH_3]}{dt} = ?$

Sol.

a.
$$H_2O_2 + 2H^{\oplus} + 3I^{\ominus} \longrightarrow I_3^{\ominus} + 2H_2O$$

The equality in this case is

$$\frac{-d\left[\mathrm{H}_{2}\mathrm{O}_{2}\right]}{dt} = \frac{1}{2} \frac{-d\left[\mathrm{H}^{\oplus}\right]}{dt} = \frac{1}{3} \frac{-d\left[\mathrm{I}^{\odot}\right]}{dt} = \frac{d\left[\mathrm{I}_{3}^{\odot}\right]}{dt}$$

$$= \frac{1}{2} \frac{d [H_2 O]}{dt}$$

So
$$\frac{-d \left[I^{\odot}\right]}{dt} = 3 \frac{-d \left[H_2 O_2\right]}{dt} = \frac{3}{2} \frac{-d \left[H^{\oplus}\right]}{dt}$$

$$= 3 \frac{d \left[I_3^{\odot} \right]}{dt} = \frac{3}{2} \frac{d \left[H_2 O \right]}{dt}$$

b.
$$16H^{\oplus} + 2MnO_4^{\ominus} + 10I^{\ominus} \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

The equality in this case is:

$$\frac{1}{16} \frac{-d \left[\mathbf{H}^{\oplus} \right]}{dt} = \frac{1}{2} \frac{-d \left[\mathbf{MnO_4}^{\odot} \right]}{dt} = \frac{1}{10} \frac{d \left[\mathbf{I}^{\odot} \right]}{dt}$$

$$= \frac{1}{2} \frac{d [Mn^{2+}]}{dt} = \frac{1}{8} \frac{d [H_2O]}{dt} = \frac{1}{5} \frac{d [I_2]}{dt}$$

So
$$\frac{-d [\text{MnO}_4^{\odot}]}{dt} = \frac{1}{8} \frac{-d [\text{H}^{\oplus}]}{dt} = \frac{1}{5} \frac{-d [\text{I}^{\odot}]}{dt}$$

$$= \frac{d [Mn^{2+}]}{dt} = \frac{1}{4} \frac{d [H_2O]}{dt} = \frac{2}{5} \frac{d [I_2]}{dt}$$

c.
$$4NH_2 + 5O_2 \longrightarrow 4NO_2 + 6H_2O$$

The equality in this case is:

$$\frac{1}{4} \frac{-d \text{ [NH_3]}}{dt} = \frac{1}{5} \frac{-d \text{ [O_2]}}{dt} = \frac{1}{4} \frac{d \text{ [NO_2]}}{dt} = \frac{1}{6} \frac{d \text{ [H_2O]}}{dt}$$

So,
$$\frac{-d [NH_3]}{dt} = \frac{4}{5} \frac{-d [O_2]}{dt} = \frac{d [NO_2]}{dt} = \frac{2}{3} \frac{d [H_2O]}{dt}$$

ILLUSTRATION 4.4

Ammonia and oxygen react at high temperature as:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

In an experiment, the rate of formation of NO is $3.6 \times 10^{-3} \,\mathrm{Ms^{-1}}$. Calculate (a) the rate of disappearance of ammonia and (b) the rate of formation of water.

Sol. For the reaction,

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

$$Rate = \frac{1}{4} \frac{-d [NH_3]}{dt} = \frac{1}{5} \frac{-d [O_2]}{dt}$$

$$= \frac{1}{4} \frac{d [NO]}{dt} = \frac{1}{6} \frac{d [H_2O]}{dt}$$

= Rate of appearance of NO
=
$$3.6 \times 10^{-3}$$
 mol L⁻¹ s⁻¹

$$= \frac{d [H_2O]}{dt}$$

From the rate equation,

$$\frac{1}{6} \frac{d \left[H_2 O \right]}{dt} = \frac{1}{4} \frac{d \left[NO \right]}{dt}$$

$$\therefore \frac{d [H_2 O]}{dt} = \frac{6}{4} \times 3.6 \times 10^{-3} = 5.4 \times 10^{-3} \text{ mol } L^{-1} \text{ s}^{-1}$$

ILLUSTRATION 4.5

The following reaction was carried out in water:

$$Cl_2 + 2I^{\odot} \longrightarrow I_2 + 2Cl^{\odot}$$

The initial concentration of I^{\odot} was 0.25 mol L^{-1} and the concentration after 10 min was 0.23 mol L^{-1} . Calculate the rate of disappearance of I^{\odot} and rate of appearance of I_2 .

The concentration of a reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction using units of time both in minutes and seconds.

 $= 0.66 \times 10^{-5} \text{ mol } L^{-1} \text{ s}^{-1}$

ILLUSTRATION 4.7

In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant?

$$BrO_3^{\circ}(aq) + 5\underline{Br}^{\circ}(aq) + 6H^{\oplus}(aq) \longrightarrow 3\underline{Br_2}(1) + 3H_2O(1)$$

$$\mathbf{a.} \frac{d[Br_2]}{dt} = \frac{5}{3} \frac{-d[Br^{\circ}]}{dt} \quad \mathbf{b.} \frac{d[Br_2]}{dt} = \frac{-d[Br^{\circ}]}{dt}$$

$$\mathbf{c.} \frac{d[Br_2]}{dt} = -\frac{d[Br^{\circ}]}{dt} \quad \mathbf{d.} \frac{d[Br_2]}{dt} = \frac{3}{5} \frac{-d[Br^{\circ}]}{dt}$$

$$BrO_3^{\ominus}(aq) + 5Br^{\ominus}(q) + 6H^{\oplus}(aq)$$

$$\longrightarrow 3Br_2(l) + 3H_2O(l)$$

$$Rate = \frac{1}{5} \frac{-d [Br^{\ominus}]}{dt} = \frac{1}{3} \frac{+d [Br_2]}{dt}$$

$$= \frac{d [Br_2]}{dt} = \frac{3}{5} \frac{-d [Br^{\ominus}]}{dt}$$

ILLUSTRATION 4.8

For the reaction

 $H_2(g) + I_2(g) \longrightarrow 2HI(g)$, the rate of disappearance of H_2 is 1.0×10^{-4} mol L⁻¹ s⁻¹. The rate of appearance of HI will be

a.
$$1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

b.
$$2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

c.
$$0.50 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

d.
$$4.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Sol.

b.
$$H_2(g) + I_2(g) \longrightarrow 2HI(aq)$$

Rate =
$$\frac{1}{1} - \frac{d[H_2]}{dt} = \frac{1}{1} - \frac{d[I_2]}{dt} = \frac{1}{2} + \frac{d[HI]}{dt}$$

Now,
$$\frac{d [H_2]}{dt} = -10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\therefore \frac{d [I_2]}{dt} = 2 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$$

ILLUSTRATION 4.9

The rate of reaction is expressed as:

$$\frac{1}{2} \frac{+d}{dt} [C] = \frac{1}{3} \frac{-d}{dt} [D] = \frac{1}{4} \frac{+d}{dt} [A] = -\frac{d}{dt} [B]$$

The reaction is:

a.
$$\frac{1}{4}$$
 A + $\frac{1}{2}$ C \longrightarrow B + $\frac{1}{3}$ D

b.
$$4A + 2C \longrightarrow B + 3D$$

c.
$$B + 3D \longrightarrow 4A + 2C$$

d. B +
$$\frac{1}{3}$$
D $\longrightarrow \frac{1}{4}$ A + $\frac{1}{2}$ C

Sol.

c. Rate =
$$\frac{1}{2} \frac{d[C]}{dt} = \frac{1}{3} \frac{-d[D]}{dt} = \frac{1}{4} \frac{d[A]}{dt} = \frac{-d[B]}{dt}$$

: Stoichiometric coefficient of B = 1

Stoichiometric coefficient of D = 3

Stoichiometric coefficient of A = 4

Stoichiometric coefficient of C = 2

Therefore, the reaction is: $B + 3D \longrightarrow 4A + 2C$

ILLUSTRATION 4.10

The term -dx/dt in the rate expression refers to the

- a. Concentration of the reactants
- b. Increase in concentration of the reactants
- c. Instantaneous rate of reaction
- d. Average rate of reaction
- Sol. c. It is an expression for instantaneous rate.

ILLUSTRATION 4.11

In a catalyst experiment involving the Haber process $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured as

Rate =
$$\frac{\Delta [NH_3]}{\Delta t}$$
 = 2.0 × 10⁻⁴ mol L⁻¹ s⁻¹

What is the rate of reaction expressed in terms of (a) N_2 (b) H_2 ?

Sol.
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\frac{-d[N_2]}{dt} = \frac{-d[H_2]}{3 dt} = \frac{+d[NH_3]}{2 dt}$$

a.
$$\therefore \frac{-d[N_2]}{dt} = \frac{1}{2} \times \frac{d[NH_3]}{dt} = \frac{1}{2} \times 2.0 \times 10^{-4}$$

$$= 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

b.
$$\frac{-d [H_2]}{dt} = \frac{3}{2} \times \frac{d [NH_3]}{dt}$$
$$= \frac{3}{2} \times 2.0 \times 10^{-4} = 3 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$$

The approach to the following equilibrium was observed kinetically from both directions:

[PtCl₄]²⁻ + H₂O
$$\rightleftharpoons$$
 [Pt(H₂O)Cl₃] $^{\circ}$ + Cl $^{\circ}$

At 25°C, it was found that at 0.3 ionic strength $-\frac{\Delta [PtCl_4]^2}{\Delta t}$ = (3.9 × 10⁻⁵ s⁻¹) [PtCl₄]²⁻

$$-(2.1 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}) [\text{Pt } (\text{H}_2\text{O})\text{Cl}_3]^{\odot} [\text{Cl}^{\odot}]$$

What is the value of k for the complexation of the fourth Cl^{\odot} by Pt(II) at 0.3 ionic strength.

Sol. At equilibrium,
$$\frac{\Delta [PtCl_4]^{2^-}}{\Delta t} = 0$$

$$\therefore (3.9 \times 10^{-5} \text{ s}^{-1}) [\text{PtCl}_4]^{2-} = (2.1 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1})$$

$$[\text{Pt } (\text{H}_2\text{O})\text{Cl}_3]^{\ominus} [\text{Cl}^{\ominus}]$$

For the reverse reaction given above

$$k = [\text{PtCl}_4]^{2-}/[\text{Pt} (\text{H}_2\text{O})\text{Cl}_3]^{\odot} [\text{Cl}^{\odot}]$$
$$= \frac{2.1 \times 10^{-3}}{3.9 \times 10^{-5}} = 54$$

ILLUSTRATION 4.13

Which of the following expressions can be used to describe the instantaneous rate of the reaction?

$$2A + B \longrightarrow A_2B$$

a.
$$\frac{1}{2} \frac{-d[A]}{dt}$$
 b. $\frac{-d[A]}{dt}$

b.
$$\frac{-d[A]}{dt}$$

c.
$$\frac{1}{2} \frac{d [A_2 B]}{dt}$$

d.
$$\frac{1}{2} \frac{-d[A]}{dt} \cdot \frac{d[B]}{dt}$$

a. The instantaneous rate of the reaction can be expressed by any of the following expressions.

$$\frac{1}{2} \frac{-d[A]}{dt}$$
 or $\frac{-d[B]}{dt}$ or $\frac{d[A_2B]}{dt}$

ILLUSTRATION 4.14

Which of the following will react at the highest rate?

- a. 1 mol of A and 1 mol B in a 1-L vessel
- b. 2 mol of A and 2 mol B in a 2-L vessel
- c. 3 mol of A and 3 mol B in a 3-L vessel
- d. All would react at the same rate

Sol.

d. Since all have same concentration of reactants all would react at same rate.

ILLUSTRATION 4.15

The reaction between $Cr_2O_7^{2-}$ and HNO_2 in an acidic medium is

$$\operatorname{Cr}_2\operatorname{O}_7^{2-} + 5\operatorname{H}^{\oplus} + 3\operatorname{HNO}_2 \longrightarrow 2\operatorname{Cr}^{3+} + 3\operatorname{NO}_3^{\ominus} + 4\operatorname{H}_2\operatorname{O}_2$$

The rate of disappearance of $Cr_2O_7^{2-}$ is found to be 2.4×10^{-4} mol L⁻¹ s⁻¹ during measured time interval. What will be the rate of disappearance of HNO₂ during the same time interval? **a.** 2.4×10^{-4} **b.** 7.2×10^{-4} **c.** 4.8×10^{-4} **d.** 0.8×10^{-4}

b. Rate =
$$\frac{dt}{dt} = \frac{3}{3} \frac{dt}{dt}$$
or
$$\frac{d [\text{HNO}_2]}{dt} = \frac{3d [\text{Cr}_2 \text{O}_7^{2-}]}{dt}$$

$$\therefore \frac{d [\text{HNO}_2]}{dt} = 3 \times 2.4 \times 10^{-4} = 7.2 \times 10^{-4}$$

ILLUSTRATION 4.16

The complexation of Fe2+ with the chelating agent dipyridyl has been studied kinetically in both the forward and reverse directions. For the complexation reaction $Fe^{2+} + 3 \text{ dipy} \rightarrow [Fe (dipy)_3]^{2+}$, the rate of formation of the complex at 25°C is given by

Rate = $(1.45 \times 10^{13} \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}) \text{ [Fe}^{2+}] \text{ [dipy]}^3$ and for the reverse of the above equation, the rate of disappearance of the complex is

$$(1.22 \times 10^{-4} \text{ s}^{-1}) [\text{Fe}(\text{dipy})_3]^{2+}]$$

What is K_s, the stability constant for the complex?

Sol. At equilibrium, the rate of forward reaction = rate of backward reaction

$$\therefore R_f = R_b$$
[1.45 × 10¹³ L³ mol⁻³ s⁻¹] [Fe²⁺] [dipy]³
= (1.22 × 10⁻⁴ s⁻¹) [Fe(dipy)₃]²⁺

$$\therefore k_{\rm s} = \frac{R_{\rm f}}{R_{\rm b}} = \frac{[{\rm Fe} \, ({\rm dipy})_3]^{2+}}{[{\rm Fe}^{2+}] [{\rm dipy}]^3} = \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}$$

Calculation of the rate of reaction in terms of change of pressure per time when the rate of one of the reactants or product is given in the terms of moles per litre per time

If the rate of reaction is given in terms of moles L^{-1} time⁻¹, the change in pressure may be derived by using gas law equation PV = nRT.

$$\therefore$$
 Moles per litre volume $\left(\frac{n}{V}\right) = \frac{P}{RT}$

Change in pressure
$$(\Delta P)$$

$$\therefore \text{ Rate of reaction} = \frac{RT}{\text{Change in time } (\Delta t)}$$

Similarly, if the rate of reaction is given in terms of pressure per time, then the rate of reaction in terms of moles per litre may. be derived as:

$$PV = nRT; \quad \frac{n}{V} = \frac{P}{RT}$$

$$\therefore \frac{\Delta(n/V)}{\Delta t} \operatorname{mol} L^{-1} t^{-1} = \frac{\Delta P}{\Delta t} \times \frac{1}{RT}$$

For the reaction at 273 K

or the reaction at 275 kg

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

It is observed that the pressure of NO(g) falls from 700 mm Hg 10 500 mm Hg in 250 s. Calculate the average rate of reaction **(b)** mol L^{-1} s⁻¹. in (a) atm s-1

Sol.
$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Change of pressure

Average rate =
$$\frac{\text{Change of pressure}}{\text{Change of time}} = \frac{\Delta P}{\Delta t}$$
$$= \frac{700 - 500}{250} = \frac{200}{250}$$
$$= \frac{200}{760 \times 250} \text{ atm s}^{-1}$$
$$= 1.053 \times 10^{-3} \text{ atm s}^{-1}$$

b.
$$\frac{\Delta(n/V)}{\Delta t} \mod L^{-1} \ t^{-1} = \frac{\Delta P}{\Delta t} \times \frac{1}{RT}$$
$$= \frac{1.053 \times 10^{-3} \text{ atm s}^{-1}}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}) (273 \text{ K})}$$
$$= 4.7 \times 10^{-5} \mod L^{-1} \text{ s}^{-1}$$

ILLUSTRATION 4.18

The hydrogenation of vegetable ghee at 25°C reduces the pressure of H₂ from 2 atm to 1.2 atm in 50 min. Calculate the rate of reaction in terms of change of

- a. Pressure per minute
- b. Molarity per second

a. Rate of reaction =
$$\frac{\text{Change in pressure}}{\text{Time in min}} = \frac{2 - 1.2}{50}$$

= $\frac{0.8}{50} = 1.6 \times 10^{-2} \text{ atm min}^{-1}$

b. : Change in molarity may be derived by PV = nRT

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} = \frac{0.8}{0.0821 \times 298} = 0.0327$$
Rate of reaction = $\frac{\text{Change in molarity}}{\text{Time in second}}$

$$= \frac{0.0327}{50 \times 60} = 1.09 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

ILLUSTRATION 4.19

For gaseous reactions, the rate is expressed in terms of dPldt instead of dc/dt or dn/dt (where c is the concentration and n the number of mol). What is the relation among these expressions?

Sol.
$$\frac{dc}{dt} = \frac{1}{V} \left[\frac{dn}{dt} \right]$$
 ...(i)

(as $c = \frac{n}{V}$, where n = number of moles, V = volume of solution)

Using gas law equation,

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

or
$$\frac{n}{V} = \frac{P}{RT}$$
 or $\frac{dn}{V} = \frac{dP}{RT}$...(ii)

Substituting Eq. (ii) in Eq. (i), we get

$$\frac{dc}{dt} = \frac{1}{RT} \left[\frac{dP}{dt} \right]$$

4.2.1 RELATION BETWEEN DIFFERENT RATE OF FORMATION/DECOMPOSITION IN MASS $TIMF^{-1}$

Relation between the rate of formation/decomposition of any one of the reactants/product given in mass time-I and the rate of formation/decomposition of another reactant/product is required in mass time⁻¹.

For general formula,

$$aA + bB \longrightarrow cC + dD$$

$$\frac{-d[A]}{a dt} = \frac{-d[B]}{b dt} = \frac{d[C]}{c dt} = \frac{d[D]}{d dt}$$

For example:

$$\therefore \frac{-d[A]}{dt} = \frac{a}{c} \frac{d[C]}{dt} \mod L^{-1} t^{-1}$$

a.
$$\frac{-d[A]}{dt}$$
 in mass $t^{-1} = \frac{a}{c} \frac{d[C]}{dt} \times \frac{Mw \text{ of } A}{Mw \text{ of } C} \text{ mass } t^{-1}$

b.
$$\frac{-d[A]}{dt}$$
 in mass $t^{-1} = \frac{a}{d} \frac{d[D]}{dt} \times \frac{Mw \text{ of } A}{Mw \text{ of } D}$ mass t^{-1}

Similarly:

c.
$$\frac{-d[B]}{dt}$$
 in mass $t^{-1} = \frac{b}{c} \frac{d[C]}{dt} \times \frac{Mw \text{ of } B}{Mw \text{ of } C} \text{ mass } t^{-1}$

d.
$$\frac{-d[B]}{dt}$$
 in mass $t^{-1} = \frac{b}{d} \frac{d[D]}{dt} \times \frac{Mw \text{ of B}}{Mw \text{ of D}} \text{ mass } t^{-1}$

For example, $N_2 + 3H_2 \longrightarrow 2NH_3$

$$\frac{-d[H_2]}{dt} = \frac{3}{2} \frac{d[NH_3]}{dt} \times \frac{Mw \text{ of } H_2}{Mw \text{ of } NH_3} \text{ mass } t^{-1}$$

Alternatively:

$$3H_2 \equiv 2NH_3$$

$$3 \times 2 \equiv 2 \times 17$$

Rate of decomposition of H₂ (to be calculated)

Rate of formation of NH₃ (given)

$$= \frac{\text{Total weight of H}_2}{\text{Total weight of NH}_3} = \frac{3 \times 2}{2 \times 17} g t^{-1}$$

In the reaction, $2H_2O_2 \longrightarrow 2H_2O + O_2$

The rate of decomposition of H_2O_2 is 0.68 kg hr⁻¹. What is the rate of formation of O_2 and H_2O in kg hr⁻¹?

Sol.
$$\frac{-d [H_2O_2]}{2 dt} = \frac{d [H_2O]}{2 dt} = \frac{d [O_2]}{dt}$$
a.
$$\frac{d [O_2]}{dt} = \frac{1}{2} \times \frac{-d [H_2O_2]}{dt} \times \frac{Mw \text{ of } O_2}{Mw \text{ of } H_2O_2}$$

$$= \frac{1}{2} \times 0.68 \text{ kg hr}^{-1} \times \frac{32 \times 10^{-3} \text{ kg}}{34 \times 10^{-3} \text{ kg}}$$

$$= 0.32 \text{ kg hr}^{-1}$$
b.
$$\frac{d [H_2O]}{dt} = \frac{2}{2} \times \frac{-d [H_2O_2]}{dt} \times \frac{Mw \text{ of } H_2O}{Mw \text{ of } H_2O_2}$$

$$\times 0.68 \text{ kg hr}^{-1} \times \frac{18 \times 10^{-3} \text{ kg}}{34 \times 10^{-3} \text{ kg}}$$

$$= 0.36 \text{ kg hr}^{-1}$$

4.2.2 FACTORS INFLUENCING THE RATE OF REACTION

There are a number of factors which influence the rate of a reaction. Some of the important factors are:

- a. Concentration of the reacting species
- b. Temperature of the system
- c. Nature of reactants and products
- d. Presence of a catalyst
- e. Surface area of reactants
- f. Presence of light

Let us briefly discuss these factors.

- a. Concentration of reactants: We know that the concentration of the reactant is maximum (Fig. 4.1) at the start of the reaction and therefore, the rate of change of concentration is also maximum. As the concentration of reactants decreases, it brings about the corresponding decrease in the rate of reaction. This means that the rate of a reaction is directly proportional to the concentration of the reactants, i.e., greater the concentration of the reactants, faster the reaction.
- b. Temperature: The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 10 K rise of temperature. In some cases, reactions do not take place at room temperature but take place at higher temperature.
- c. Nature of reactants and the products: The rates of reaction are influenced by the nature of reactants and products. A chemical reaction involves the breaking of old bonds and formation of new bonds. The reactivity of a substance can, therefore, be related to the ease with which the specific bonds are broken or formed and the number of such bonds involved. For example, the oxidation of nitric oxide to nitrogen dioxide takes place fairly rapidly while

the oxidation of carbon monoxide to carbon disoxide takes place slowly:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$(fast)$$

$$(slow)$$

In the above reactions, the reacting species appear to be very similar to each other, still they differ in reaction rates.

- d. Presence of catalyst: A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.
- e. Surface area of the reactants: The larger the surface area of the reactants, the faster is the rate of reaction. For a reaction involving a solid reactant or catalyst, the rate of reaction depends upon the state of sub-division of the solid, the smaller the particle size, i.e., greater is the surface area, the faster is the reaction.
- f. Presence of light: In some case, the rate of a chemical reaction is considerably increased by the use of certain radiations. The photons of these radiations having frequencies (v) possess sufficient energies (E = hv) to break certain bonds in reactants. For example, the reaction of hydrogen and chlorine takes place very slowly in the absence of light. However, in the presence of light, the reaction takes place very rapidly.

4.2.3 RATE EXPRESSION AND RATE CONSTANT

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and sometimes even on the concentration of products or some foreign substances. The representation of rate of a reaction in terms of the concentration of the reactants is called rate law. The rate law for a given reaction has to be established by experimental study of the rate of reaction over a wide range of concentration of the reactants and products. The rate law thus established is also called *differential rate equation* or *rate expression*.

Figure 4.2 clearly shows that the rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Conversely, rates generally increase when reactant concentrations increase. So, the rate of a reaction depends upon the concentration of reactants.

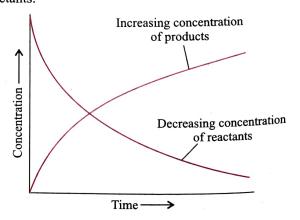


Fig. 4.2 Graph of concentration versus time

Let us consider a general reaction

Let us consider
$$aB \longrightarrow cC + dD$$

where a, b, c, and d are the stoichiometric coefficients of reactants and products.

Rate
$$\propto [A]^x [B]^y$$
 ...(i)

where exponents x and y may or may not be equal to the where a and b of the reactants. The above stoichiometric coefficients (a and b) of the reactants. equation can also be written as

Rate =
$$k [A]^x [B]^y$$
 ...(ii)

$$-\frac{d[R]}{dt} = k[A]^{x}[B]^{y} \qquad ...(iii)$$

This form of Eq. (iii) is known as differential rate equation, where k is a proportionality constant called *rate constant*. The equations such as (ii) and (iii) which relates the rate of a reaction to the concentration of reactants is called rate law or rate expression. Thus, rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Now, if the concentration of each of the reactants involved in the reaction is unity, i.e., [A] = [B] = 1, then substituting these value in the above expression, we get

Rate of reaction =
$$k \times 1 \times 1 = k$$

Thus, the rate constant of a reaction at a given temperature may be defined as the rate of the reaction when the concentration of each of the reactants is unity.

Characteristics of rate constant

The characteristics of rate constant are as follows:

- a. Rate constant is a measure of the rate of reaction. Larger the value of k, faster is the reaction. Similarly, smaller value of k indicates slower reactions.
- **b.** Different reactions have different values of k.
- c. At a fixed temperature, the value of k is constant and is characteristic of a reaction. However, it changes with temperature.
- d. For a particular reaction, the rate constant is independent of concentration.

4.2.4 DIFFERENCE BETWEEN RATE OF REACTION AND REACTION RATE CONSTANT

Following are the differences between rate of reaction and reaction rate constant:

	Rate of reaction	Reaction rate constant
1.	It is the speed with which reactants are converted into products. It is measured as the rate of decrease in the concentration of reactants with time.	It is the proportionality constant in the rate law and is defined as the rate of reaction when the concentration of the reactants is unity.

	initial concentration of reactants.	It is independent of the initial concentration of reactants.
3.	Its units are always mol L^{-1} time ⁻¹ .	Its units depend upon the order of reaction.

It may be noted that the rate law gives the experimentally observed dependence of rate on the concentration of reactants.

The powers of concentrations of reactants in rate law expression may or may not be same as the coefficient of reaction in the balanced chemical equation. Thus, we can say that:

Rate law for any reaction cannot be predicted by merely looking at the balance chemical equation, i.e., theoretically but must be determined experimentally.

Some examples are given below:

	Reaction	Experimental rate expression
1.	$2NO(g) + O_2(g)$ $\longrightarrow 2NO_2(g)$	Rate = $k [NO_2]^2 [O_2]$
2.	$\begin{array}{c} \text{CHCl}_3 + \text{Cl}_2 \\ \longrightarrow \text{CCl}_4 + \text{HCl} \end{array}$	Rate = k [CHCl ₃] [Cl ₂] ^{1/2}
3.	$CH_3COOC_2H_5 \longrightarrow CH_3COOH + C_2H_5OH$	Rate = k $[CH_3COOC_2H_5]^1[H_2O]$

4.3 ORDER OF REACTION

Let us consider a general reaction

$$aA + bB \longrightarrow Product$$

The rate of reaction is given as:

Rate =
$$k [A]^x [B]^y$$
 ...(i)

where x and y indicate how sensitive the rate is to the change in the concentration of A and B. The sum of these exponents, i.e., n = x + y gives the overall order of a reaction whereas x and y represents the order with respect to the reactants A and B, respectively. Hence, the sum of powers of the concentration of the reactants in the rate law expression determined experimentally is called the order of that chemical reaction.

The order of a reaction can be 0, 1, 2, 3, and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called elementary reactions. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions.

These may be consecutive reactions (e.g., oxidation of ethane to CO2 and H2O passes through a series of intermediate steps in which alcohol, aldehyde, and acid are formed), reverse reactions; and side reactions (e.g., nitration of phenol yields o-nitrophenol and p-nitrophenol). In an elementary reaction, the reaction takes place in one step. The reaction between H_2 and I_2 is an elementary reaction as H_2 and I_2 molecules collide together and separate out as 2 HI molecules.

At high temperature and in the presence of light, the reaction is no longer an elementary reaction and involves iodine atoms.

On the other hand, the reaction between H₂ and Br₂ is a complex reaction that takes place in a number of steps involving both Br and H atoms.

The definition of the order of reaction is valid both for elementary and complex reactions and the order of a reaction has always to be determined experimentally.

Unit of rate constant

We have noted earlier the dimensions of rate are equal to concentration/time. The SI units for concentration are mol m^{-3} , mol dm^{-3} , or mol L^{-1} and seconds for time but other units are used depending on how fast or slow is the reaction. For very slow reactions, time may be chosen in years and for very fast reactions it may be chosen in nano (10^{-9}) or pico (10^{-12}) seconds.

For the *n*th order of a reaction:

$$nA \longrightarrow Product$$

Rate =
$$k[A]^n$$
.

$$\therefore k = \frac{\text{Rate}}{[A]^n}$$

Thus, the dimensions of k are equal to

$$\frac{\text{Concentration/Time}}{[\text{Concentration}]^n} = [\text{Concentration}]^{1-n} [\text{Time}]^{-1}$$

where n =order of reaction.

Taking SI units of concentration (mol L^{-1}) and time (s), the units of k for different reaction order are listed in Table 4.1.

Table 4.1 Units of rate constant

	Reaction	Order	Units of rate constant
a.	Zero order reaction	0	$\frac{(\text{mol } L^{-1})}{s} \times \frac{1}{(\text{mol } L^{-1})^0} = \text{mol } L^{-1} s^{-1}$
b.	First order reaction	1	$\frac{(\text{mol } L^{-1})}{s} \times \frac{1}{(\text{mol } L^{-1})^1} = s^{-1}$
c.	Second order reaction	2	$\frac{(\text{mol } L^{-1})}{s} \times \frac{1}{(\text{mol } L^{-1})^2} = \text{mol}^{-1} L s^{-1}$
d.	nth order reaction	n	$\frac{(\text{mol } L^{-1})}{s} \times \frac{1}{(\text{mol } L^{-1})^n}$
			= $(\text{mol/L})^{1-n} s^{-1}$ = $\text{mol}^{1-n} L^{n-1} s^{-1}$

Units of rate constants for gaseous reactions

In case of gaseous reactions, concentrations are expressed in terms of pressure in the units of atmosphere. Therefore, the rate has the

units of atm per second. Thus, the unit of different rate constants would be

a. Zero order reactions : $atm s^{-1}$

b. First order reactions : s^{-1}

c. Second order reactions : atm⁻¹ s⁻¹

d. Third order reaction : $atm^{-2} s^{-1}$ $atm^{(1-n)} s^{-1}$

e. nth order reaction : $atm^{(1-n)}s^{-1}$ The value of rate constant depends upon the following

- a. Nature of reactant
- b. Temperature
- c. Catalyst

factors:

Initial Rate Method

ILLUSTRATION 4.21

For a reaction

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g),$$

the following data were obtained:

	[NO] (mol L ⁻¹)	$[H_2]$ (mol L^{-1})	Rate (mol L ⁻¹ s ⁻¹)
1.	5 × 10 ⁻³	2.5×10^{-3}	3 × 10 ^{−5}
2.	15×10^{-3}	2.5×10^{-3}	9×10^{-5}
3.	15×10^{-3}	10×10^{-3}	3.6×10^{-4}

- a. Calculate the order of reactions.
- b. Find the rate constant.
- c. Find the initial rate if [NO] = $[H_2] = 8.0 \times 10^{-3} M$

Sol.

a. Assuming rate law can be expressed as follows:

 $rate = k [NO]^x [H_2]^y$

By analyzing the data:

From observations 1 and 2, we see that $[H_2]$ is constant and when [NO] is tripled, the rate is also tripled.

Rate \propto [NO] $\Rightarrow x = 1$

From observations (2) and (3), we see that [NO] is constant; when [H₂] is increased four times, the rate also increases four times.

Rate \propto [H₂] \Rightarrow $y = 1 \Rightarrow r = k$ [NO] [H₂O]

The order of reaction w.r.t. NO and H_2 is 1 and the overall order of reaction is 1 + 1 = 2

b. Rate = k [NO] [H₂] or using (1)

$$3 \times 10^{-5} = k (5 \times 10^{-3}) (2.5 \times 10^{-3}) \text{ or } k = 2.4$$

c. Initial rate = k [NO] [H₂] = 2.4 × (8 × 10⁻³)(8 × 10⁻³) = 1.536 × 10⁻⁴ mol L⁻¹ s⁻¹

ILLUSTRATION 4.22

From the rate laws for the reactions given below, determine the order with respect to each species and the overall order:

a.
$$2HCrO_4^{\odot} + 6l^{\odot} + 14H^{\oplus} \longrightarrow 2Cr^{3+} + 3I_2 + 8H_2O$$

Rate =
$$k [HCrO_4^{\odot}] [I^{\odot}]^2 [H^{\oplus}]^2$$

b.
$$H_2O_2 + 2I^{\odot} + 2H^{\oplus} \longrightarrow I_2 + 2H_2O$$

Rate = $k [H_2O_2] [I^{\odot}]$



- The order of the reaction with respect to [HCrO₄©] is 1: with respect to $[I^{\odot}]$ is 2, and with respect to $[H^{\oplus}]$ is 2. The overall order of the reaction is 1 + 2 + 2 = 5.
- The order of the reaction with respect to [H₂O₂] is 1 and with respect to $[I^{\odot}]$ is 1. The overall order of the reaction is 1 + 1 = 2.

The rate constant for the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is $\frac{2}{3.0 \times 10^{-5}}$ s⁻¹. If the rate is 2.40×10^{-5} mol L⁻¹ s⁻¹, then the initial concentration of N₂O₅ (in mol L⁻¹) is

- a. 1.4
- **b.** 1.2 **c.** 0.04
- d.0.8

Sol.

d. Rate = $k [N_2O_5]$ $2.4 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} = (3.0 \times 10^{-5} \text{ s}^{-1}) [\text{N}_2\text{O}_5]$ $[N_2O_5] = \frac{2.4 \times 10^{-5} \text{ mol } L^{-1} \text{ s}^{-1}}{3.0 \times 10^{-5} \text{ s}^{-1}} = 0.8 \text{ mol } L^{-1}$

Since the unit of k is s^{-1} , hence the decomposition of N_2O_s is first order reaction.

ILLUSTRATION 4.24

The decomposition of ammonia on platinum surface follows the change

$$2NH_3 \longrightarrow N_2 + 3H_2$$

- a. What does $\frac{-d [NH_3]}{dt}$ denote?
- b. What does $\frac{d[N_2]}{dt}$ and $\frac{d[H_2]}{dt}$ denote?
- c. If the decomposition is zero order then what are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ M s}^{-1}$?
- **d.** If the rate obeys $-\frac{d [NH_3]}{dt} = \frac{k_1[NH_3]}{1 + k_2[NH_3]}$, what will be

the order for decomposition of NH3, if (i) [NH3] is very less and (ii) $[NH_3]$ is very high? $(k_1 \text{ and } k_2 \text{ are constants})$

Sol.

- a. The rate of decomposition of NH₃.
- **b.** The rate of formation of N_2 and rate of formation of H_2 .

c.
$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k[NH_3]^0$$

$$\frac{d[N_2]}{dt} = k = 2.5 \times 10^{-4} \text{ M s}^{-1}$$

$$\frac{d[H_2]}{dt} = 3k = 3 \times 2.5 \times 10^{-4} = 7.5 \times 10^{-4} \text{ M s}^{-1}$$

d.
$$-\frac{d [NH_3]}{dt} = \frac{k_1 [NH_3]}{1 + k_2 [NH_3]}$$

If $[NH_3]$ is very low, then $k_2[NH_3]$ can be neglected compared to unity and we have,

$$\frac{-d [NH_3]}{dt} = k_1 [NH_3], \text{ i.e., first order reaction w.r.t.}$$

$$NH_3.$$

If [NH3] is very high, we may neglect unity compared to $k_2[NH_3]$ and we have,

$$\frac{-d[NH_3]}{dt} = \frac{k_1[NH_3]}{k_2[NH_3]} = \frac{k_1}{k_2} = k$$

It can be seen that the rate is constant, a characteristic of zero order reaction.

ILLUSTRATION 4.25

The rate constant for the reaction:

$$CO_2 + \stackrel{\bigcirc}{OH} \longrightarrow HCO_3 \stackrel{\bigcirc}{O}$$

in the aqueous solution is 4×10^{-3} L mol⁻¹ s⁻¹. Calculate the number of mole of CO₂ and OH used up per second when [CO₂] and [OH] are 10^{-6} and 10^{-1} mol L⁻¹. Also predict the mole of HCO₃[⊙] formed per second.

Sol. Rate of reaction =
$$\frac{-d [CO_2]}{dt} = \frac{-d [OH]}{dt} = \frac{d [HCO_3]}{dt}$$

Also the unit of k suggests it to be II order. Thus, rate of reaction

=
$$k \text{ [CO}_2$$
] [OH] = $4 \times 10^{-3} \times 10^{-6} \times 10^{-1}$
= $4 \times 10^{-10} \text{ mol L}^{-1} \text{ s}^{-1}$

ILLUSTRATION 4.26

For a reaction 3A ----- Products, it is found that the rate of reaction doubles. If the concentration of A is increased four times, calculate the order of reaction.

Sol. Rate =
$$k$$
 [Reactant] ^{n} ; if [Reactant] = a , rate = r_1
 $r_1 = k$ [a] ^{n} if [Reactant] = $4a$, rate = $2r_1$
 $2r_1 = k$ [$4a$] ^{n}
 $\frac{1}{2} = \left[\frac{1}{4}\right]^n \Rightarrow n = \frac{1}{2}$

ILLUSTRATION 4.27

The rate of a reaction starting with initial concentration of 2×10^{-3} and 1×10^{-3} M are equal to 2.40×10^{-4} and $0.60 \times 10^{-4} \text{ M s}^{-1}$; respectively. Calculate the order or reaction w.r.t. reactant and also the rate constant.

Sol.
$$(r_0)_1 = k [A_0]_1^a$$
 (a is order of reaction)
 $(r_0)_2 = k [A_0]_2^a$
 $\frac{(r_0)_1}{(r_0)_2} = \left\{ \frac{[A_0]_1}{[A_0]_2} \right\}^a$

or
$$a = \frac{\log (r_0)_1 - \log (r_0)_2}{\log [A_0]_1 - \log [A_0]_2}$$

$$= \frac{\log [2.40 \times 10^{-4}] - \log [0.60 \times 10^{-4}]}{\log [2 \times 10^{-3}] - \log [1 \times 10^{-3}]}$$

$$= \frac{-3.62 + 4.22}{-2.70 + 3} = 2$$

$$r = k [A]^2$$

$$r = k [A]^{2}$$
Also, $k = \frac{r}{[A]^{2}} = \frac{2.40 \times 10^{-4}}{[2 \times 10^{-3}]^{2}} = 60 \text{ mol}^{-1} \text{ L s}^{-1}$

The reaction $2A + B + C \longrightarrow D + 2E$ is found to be first order in A, second order in B and zero order in C.

- a. Write the rate expression.
- b. What is the effect on rate on increasing the concentration of A, B, and C two times?

Sol.

- **a.** Rate = $k [A]^1 [B]^2 [C]^0$
- **b.** Let the initial concentration of A, B and C be a, b, and $c \text{ mol } L^{-1}$, respectively.

Then, rate
$$r_1 = k a^1 b^2 c^0$$
 ...(i)

Now if concentrations of A, B, and C are doubled, i.e., 2a, 2b, and 2c, respectively.

$$r_2 = k(2a)^1(2b)^2(2c)^0$$
 ...(ii)

By Eqs. (i) and (ii),
$$\frac{r_1}{r_2} \doteq \frac{1}{8} : r_2 = 8r_1$$
.

ILLUSTRATION 4.29

For $2A + B + C \longrightarrow Products$, calculate:

- a. Rate expression, using rate law.
- b. Units of rate and rate constant.
- c. Effect on rate, if the concentration of A is doubled and that of B is tripled.

Sol.

- **a.** Rate = $k [A]^2 [B]^1 [C]^0$ (Since C is in excess)
- **b.** Unit of rate = mol L^{-1} time⁻¹

Unit of rate constant for third order = $L^2 \text{ mol}^{-2} \text{ time}^{-1}$

c. Let initial concentration of A, B, and C be a, b, and c, respectively.

$$\therefore r_1 = k(a)^2(b)^1(c)^0$$

Now,
$$[A] = 2a$$
; $[B] = 3b$

$$r_2 = K (2a)^2 (3b)^1 (c)^0$$
 ...(ii)

By Eqs. (i) and (ii),
$$\frac{r_1}{r_2} = \frac{1}{12}$$
 : $r_2 = 12r_1$

ILLUSTRATION 4.30

The rate of reaction: $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$, becomes doubled when the concentration of Cl₂ is doubled. However, when the concentration of both the reactants are doubled, the rate becomes eight times. What is the order w.r.t. NO and w.r.t. chlorine? What is the total order?

Sol.
$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Let the rate of reaction is

$$r_1 = k[\text{NO}]^{\alpha}.[\text{Cl}_2]^{\beta} \qquad \dots \text{(i)}$$

$$r_1 = k[NO]^{\alpha} \cdot [2Cl_2]^{\beta}$$
 ...(ii)

$$r_2 = 2r_1 - k[1 - 3]^{\alpha}$$

 $r_3 = 8r_1 = k[2NO]^{\alpha} \cdot [2Cl_2]^{\beta}$...(iii)

$$r_3 = 8r_1 = k [2NO]^{\frac{1}{4}} \cdot \frac{2^3}{2^3}$$

$$\frac{r_2}{r_1} = \frac{2r_1}{r_1} = \frac{k[NO]^{\frac{3}{4}} \cdot [2Cl_2]^{\frac{3}{4}}}{k[NO]^{\frac{3}{4}} \cdot [Cl_2]^{\frac{3}{4}}} \quad \therefore (2)^1 = (2)^{\beta}$$

$$\beta = 1$$

Similarly, divide Eq. (iii) by Eq. (i)

$$\frac{r_3}{r_1} = \frac{8r_1}{r_1} = \frac{k[2\text{NO}]^{\acute{a}}.[2\text{Cl}_2]^{\acute{a}}}{k[\text{NO}]^{\acute{a}}.[\text{Cl}_2]^{\acute{a}}}$$

$$8 = (2)^{\alpha} \cdot (2)^{\beta}$$

$$8 = (2)^{\alpha} \cdot (2)^{1}$$

$$4 = (2)^{\alpha}$$

$$(2)^2 = (2)^\alpha$$

$$\alpha = 2$$

$$\therefore r = k [NO]^2 [Cl_2]^1$$

Order w.r.t.
$$NO = 2$$

$$\therefore$$
 Order w.r.t. $Cl_2 = 1$

Overall order of reaction = 2 + 1 = 3

ILLUSTRATION 4.31

Show by using rate laws how much the rate of reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ will change if the volume of the reaction vessel is diminished to 1/3 of its initial volume.

Sol.
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Using rate law, as given theoretically, i.e.,

$$r_1 = k[\text{NO}]^2[\text{O}_2]$$

When the volume is reduced to one-third of initial value, the concentration or partial pressure becomes three times.

:.
$$r_2 = k [3NO]^2 [3O_2]$$

$$\therefore \frac{r_2}{r_1} = 27$$

$$r_2 = 27r_1$$

...(i)

ILLUSTRATION 4.32

What would be the effect on the rate of reaction due to the fourfold increase in a reactant concentration, if the order of reaction were the following:

- a. Zero order
- b. First order
- c. 1/2 order
- d. Fourth order



a.
$$r_1 = k[A]^n$$

When $n = 0$

$$r_1 = k[A]^0$$

$$r_2 = k[4A]^0$$

$$\frac{r_2}{r_1} = r_2$$
, (No change in rate)

$$\mathbf{b}. \quad r_1 = k[A]^n,$$

When
$$n = 1$$
, $r_1 = k[A]^1$, $r_2 = k[4A]^1$

$$\frac{r_2}{r_1} = \frac{k \times 4 \left[A\right]^1}{k \times \left[A\right]^1}$$

$$r_2 = 4r_1 \Rightarrow 4 \text{ times}$$

c. When
$$n = \frac{1}{2}$$
, $r_1 = k[A]^{\frac{1}{2}}$, $r_2 = k[4A]^{\frac{1}{2}}$

$$\frac{r_2}{r_2} = (4)^{1/2}$$

$$\therefore r_2 = 2r_1 \Rightarrow 2 \text{ times}$$

d.
$$r_1 = k[A]^4$$
; $r_2 = k[4A]^4$; when $n = 4$

$$\frac{r_2}{r_1} = \frac{k[4]^4 [A]^4}{k[A]^4}$$

$$r_2 = 256r_1 \Rightarrow 256 \text{ times}$$

The experimental rate law for the reaction $S_2O_8^{2-}(aq) + 2I^{\odot}(aq)$ \longrightarrow 2SO₄²-(aq) + I₂(aq) is

 $k[S_2O_8^{2-}][I^{\odot}]$. How would the rate change if

- a. Concentration of S₂O₈²⁻ is halved.
- **b.** Concentration of $S_2O_8^{2-}$ and I^{\odot} are halved.

a.
$$r_1 = k [S_2 O_9^{2-}] [I^{\odot}]$$

$$r_2 = k \left[\frac{S_2 O_8^{2-}}{2} \right] [I^{\odot}]$$

$$\frac{r_2}{r_1} = \frac{1}{2} \Rightarrow r_2 = \frac{1}{2} r_1$$

b.
$$r_2 = k \left[\frac{S_2 O_8^{2-}}{2} \right] \left[\frac{I^{\odot}}{2} \right]$$

$$\frac{r_2}{r_1} = \frac{1}{4}$$

ILLUSTRATION 4.34

For the reaction $A + B \longrightarrow C + D$, doubling the concentration of both the reactants increases the reaction rate by 8 times and doubling the initial concentration of only B simply doubles the reaction rate. What is the rate law for the reaction?

Sol. For the reaction $A + B \longrightarrow C + D$

Rate of reaction:

$$r_1 = k[A]^x [B]^y \qquad \dots (i)$$

$$r_2 = 8r_1 = k[2A]^x [2B]^y$$
 ...(ii)

$$r_3 = 2r_1 = k[A]^x [2B]^y$$
 ...(iii)

Dividing Eq. (iii) by Eq. (i),

$$\frac{2r_1}{r_1} = \frac{k[A]^x [2B]^y}{k[A]^x [B]^y}$$

$$(2)^1 = (2)^y$$
 or $y = 1$

Dividing Eq. (ii) by Eq. (i),

$$\frac{8r_1}{r_2} = \frac{k[2A]^x [2B]^y}{k[A]^x [B]^y}$$

$$8 = (2)^x (2)^y$$

$$8 = (2)^x (2)^1$$

$$4 = (2)^x$$

$$(2)^2 = (2)^x$$

$$x = 2$$

$$\therefore r = k[A]^2 [B]$$

ILLUSTRATION 4.35

For the non-equilibrium process, $A + B \longrightarrow Product$, the rate is first order w.r.t. A and second order w.r.t. B. If 1.0 mol each of A and B were introduced into 1.0 L vessel and the initial rate was 1.0×10^{-2} mol L⁻¹ s⁻¹, calculate the rate when half the reactants have been turned into products.

Sol. $r = k[A] [B]^2$

$$10^{-2} = k[1.0] [1.0]^2$$

$$k = 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

When half of the reactants have been turned into products, the concentration of A and B left are 0.5 mol.

$$\therefore r = k[0.5] [0.5]^2 = 10^{-2} \times 0.5 \times 0.5 \times 0.5$$

$$= 1.25 \times 10^{-3} \text{ mol } L^{-1} \text{ s}^{-1}$$

ILLUSTRATION 4.36

The rate constant is numerically the same for three reactions of first, second, and third order. Which reaction should be the fastest and is this true for all ranges of concentrations?

Sol. $A \longrightarrow Product$

$$r_1 = k$$
 [A] for first order

$$r_2 = k [A]^2$$
 for second order

$$r_3 = k [A]^3$$
 for third order

k is same in all.

If [A] = 1,
$$r_1 = r_2 = r_3$$

If [A] < 1,
$$r_1 > r_2 > r_3$$

If [A] > 1,
$$r_3 > r_2 > r_1$$

ILLUSTRATION 4.37

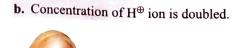
The rate law for the following reactions:

Ester +
$$H^{\oplus}$$
 \longrightarrow Acid + Alcohol, is

$$dx/dt = k(\text{ester}) [H_3 O^{\oplus}]^0$$

What would be the effect on the rate if

a. Concentration of ester is doubled.



Sol.

a. $r = k \text{ [Ester]}^1 \text{ [H}_3 \text{O}^{\oplus} \text{]}^0$

$$r_1 = k [a]^1 [b]^0$$

$$r_2 = k [2a]^1 [b]^0$$

$$\frac{r_1}{r_2} = \frac{1}{2}, \ r_2 = 2r_1$$

- **b.** $r_3 = k [a]^1 [2b]^0$
 - $\frac{r_1}{r_3} = 1, r_1 = r_3$

CONCEPT APPLICATION EXERCISE 4.1

1. A reaction, $3X \longrightarrow 2Y + Z$ proceeds in a closed vessel. The rate of disappearance of X, $-\Delta[X]/\Delta t$ is found to be 0.072 mol L^{-1} s⁻¹. Calculate

$$\frac{\Delta[Y]}{\Delta t}$$
 and $\frac{\Delta[Z]}{\Delta t}$.

- 2. A chemical reaction $2A \rightleftharpoons 4B + C$ in gas phase occurs in a closed vessel. The concentration of B is found to be increased by 5×10^{-3} mol L⁻¹ in 10 s. Calculate (i) the rate of appearance of B and (ii) the rate of disappearance of A.
- 3. The rate of formation of second order dimerization reaction is 5.8×10^{-6} mol L⁻¹ s⁻¹ at 0.01 mol L⁻¹ monomer concentration. Calculate the rate constant.
- **4.** How can we express the rates of the following reactions in terms of concentration of reactants and products?
 - **a.** $2O_3 \Longrightarrow 3O_2$
 - **b.** $2NO + Br_2 \rightleftharpoons 2NOBr$
 - c. $2ICl(g) + H_2(g) \longrightarrow I_2(g) + 2HCl(g)$
- 5. For the reaction,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

the rate of reaction measured as $\frac{\Delta [NH_3]}{\Delta t}$ was found to

be 2.4×10^{-4} mol L⁻¹ s⁻¹. Calculate the rate of reaction expressed in terms of (a) N₂ and (b) H₂.

- 6. The reaction $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$ takes place in a closed container. It is found that the concentration of NO_2 increases by 1.6×10^{-2} mol L⁻¹ in 4 s. Calculate the rate of reaction and the rate of change of concentration of N_2O_5 .
- 7. For a reaction: 2P + Q S, following data were collected.

	P(mol L ⁻¹)	Q(mol L ⁻¹)	Rate (mol I -1 . 1
i.	6×10^{-2}	1×10^{-2}	Rate (mol L ⁻¹ min ⁻¹)
ii.	6×10^{-2}	2×10^{-2}	0.0012
iii.	12 × 10 ⁻²	1×10^{-2}	0.0024
Cal	- 1		0.0024

Calculate the overall order of the reaction. Also find out the reaction rate constant.

Initial [A] in (mol L ⁻¹)	Initial [B] in (mol L ⁻¹)	rate (mol L ⁻¹ min ⁻¹
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

What is the rate law?

- 9. A 22.4-L flask contains 0.76 mm of O₃ at 25°C. Calculate:
 - a. The concentration of oxygen atoms needed so that the reaction

$$O + O_3 \longrightarrow 2O_2$$

having rate constant $(k) = 1.5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1} \text{ can}$ proceed with a rate of 0.15 mol L⁻¹ s⁻¹.

b. The rate of formation of O₂ under this condition.

ANSWERS

- 1. $\frac{d[Y]}{dt} = 0.008 \text{ mol } L^{-1} \text{ s}^{-1}$ $\frac{d[Z]}{dt} = 0.024 \text{ mol } L^{-1} \text{ s}^{-1}$
- **2. a.** $1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- **b.** $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- 3. $5.8 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
- **4. a.** $\frac{1}{2} \frac{-d [O_3]}{dt} = \frac{1}{3} \frac{d [O_2]}{dt}$
 - **b.** $\frac{1}{2} \frac{-d \text{ [NO]}}{dt} = \frac{1}{2} \frac{-d \text{ [Br}_2]}{dt} = \frac{1}{2} \frac{d \text{ [NOBr]}}{dt}$
 - **c.** $\frac{1}{2} \frac{-d \text{ [ICl]}}{dt} = \frac{-d \text{ [H}_2\text{]}}{dt} = \frac{d \text{ [I}_2\text{]}}{dt} = \frac{1}{2} \frac{d \text{ [HCl]}}{dt}$
- **5. a.** $1.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- **b.** $3.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- **6.** Rate = $1.0 \times 10^{-3} \text{ M s}^{-1}$

$$\frac{d [N_2 O_5]}{dt} = 0.5 \times 10^{-3} \text{ M s}^{-1}$$

- 7. $k = 2 \text{ L mol}^{-1} \text{ min}^{-1}$
- **8.** Rate = k [A] [B]⁰

9. a. 4.5 mm

b. 0.30 M s^{-1}

4.4 MOLECULARITY OF REACTION

Most chemical reactions proceed through a series of elementary reactions. These elementary steps are classified according to the number of molecules which they involve. Thus, the number of reacting species (atoms, ions, or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reactions is called the molecularity of a reaction. Hence, the molecularity is simply the sum of molecules of different reactions as represented by the balanced chemical equation, for example, decomposition of ammonium nitrite is unimolecular.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$$2HI \longrightarrow H_2 + I_2$$

$$\frac{\text{2NO} + O_2}{2NO + O_2} \rightarrow 2NO_2$$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than 3 is not observed.

It is, therefore, evident that complex reactions involving more than three molecules in a stoichiometric equation must take place in more than one step.

Since each elementary step involves quite different type of reactions, so each step will occur at its own distinctive rate. Some of the steps will be very fast while others will be slow. If one step takes place much more slowly than all other steps, it will definitely control the overall reaction rate. This is called the rate-determining step.

The concept of the rate-determining step is similar to that of a car factory. The different sections of the factory manufacture different parts such as engine, seats, car body, etc. The rate of production of cars per day depends upon the slowest working section of the factory. Thus, the molecularity of a reaction must always be a a whole number whereas the order of reaction can be zero or fractional also. Generally, in a complex reaction, the order of reaction is equal to the molecularity of the slowest step, yet the order of any reaction (elementary or complex) is always determined experimentally to find out the exact power of the molar concentration of each reactant on which the rate of reaction actually depends.

Generally, the order of an elementary reaction is equal to its molecularity. However, if the conditions of pressure or concentration are changed, the order may not be equal to the molecularity because in that case the reaction may not take place in one step, i.e., may not remain an elementary reaction, but may become a complex reaction. For example, a unimolecular raction is of first order at high pressure but at low pressure, it becomes of second order.

Table 4.2 Difference between molecularity and order of a reaction

Molecularity	Order
1. It is the number of reacting species undergoing simultaneous collision in an elementary or simple reaction.	1. It is the sum of powers of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentration in the rate law equation.

2. It is a theoretical concept and can be calculated by by simply adding the mole- cules of the solwest step.	2. It is determined experimentally only and cannot be calculated.
3. It is always a whole number value only, i.e., 1, 2, 3, etc.	3. It need not to be a whole number, i.e., it can be fractional zero or integer.
4. It is applicable for elementary reactions and has no meaning for complex reactions, i.e., it is only the slowest step whose molecularity has significance for the overall reactions.	4. It is applicable for both elementary as well as
5. For simple reactions, it can be obtained from the stoichiometry of the equation.	5. Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the balanced equation.
ty \geq 4 are rare.	6. Reactions with order ≥ 4 are also rare.
7. It is independent on pressure and temperature.	7. It depends upon pressure and temperature.

Note: For an elementary reaction, the order of reaction should be equal to the molecularities, and further molecularities should be integral.

For example, the rate law for the reaction:

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

is
$$\frac{d \text{ [HBr]}}{dt} = k[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}$$

If the reaction were elementary, the reaction rate would involve one molecule of H2 reacting with one molecule of Br₂ to give the bimolecular rate law.

$$\frac{d [HBr]}{dt} = k[H_2][Br_2]$$

Since this is not the observed rate law, the reaction is not elementary.

4.5 ELEMENTARY AND COMPLEX REACTIONS

The rate of reaction does not depend upon stoichiometric coefficients of the reactant in a balanced chemical equation. In other words, a balanced chemical equation does not give a true picture of how a reaction takes place. Thus, it is rare that the reaction may completed in one step.

The reactions taking place in one step are called *elementary* reactions. The reactions which do not take place in one step are called *complex reactions*. The different steps in which a complex reaction takes place is called a the mechanism of a reaction. Each step of the mechanism of a reaction is an *elementary reaction*.

According to the "collision theory," a reaction takes place when the atoms, ions, or molecules of the reactants come closer together simultaneously and collide with one another.

4.5.1 Types of Elementary Reactions

In many reaction mechanism, the following type of elementary reactions are involved:

- a. Opposed or reversible elementary reactions
- b. Side or concurrent elementary reactions
- c. Consecutive or sequential reactions

Opposed or Reversible Elementary Reactions

Opposed or reversible elementary reactions are those reactions in which both forward and backward reactions take place simultaneously. At the start, the rate of forward reaction is very large and it diminishes as the concentrations of reactants decrease with time. On the other hand, initially the rate of backward reaction is slow and it increases as the concentration of products increases with time. Very soon a stage is reached where the rate of forward reaction becomes equal to that of backward reaction and thus no further net progress is observed. This state is known as equilibrium state.

Let us consider a reversible reaction:

$$A \stackrel{k_f}{\rightleftharpoons} B$$

where k_f and k_b are rate constants of forward and backward reactions, respectively.

The rate at which the reaction proceeds will be given by

Rate or reaction = Rate of forward reaction - Rate of backward reaction

i.e.,
$$\frac{-d[A]}{dt} = \frac{d[B]}{dt} = k_f[A] - k_b[B]$$
 ...(i)

Let the reaction be started with only reactant A.

Then at time (t)

$$[A]_{0} = [A] + [B] \text{ or } [B] = [A]_{0} - [A]$$
or
$$\frac{-d[A]}{dt} = k_{f}[A] - k_{b}([A]_{0} - [A])$$

$$\frac{-d[A]}{dt} = (k_{f} + k_{b})[A] - k_{b}[A]_{0}$$

At equilibrium

$$\frac{d[A]}{dt}$$
 = 0, hence Eq. (i) reduces to

$$k_{\rm f} [{\rm A}]_{\rm eq} = k_{\rm b} [{\rm B}]_{\rm eq}$$
or
$$k_{\rm eq} = \frac{k_{\rm f}}{k_{\rm b}} = \frac{[{\rm B}]_{\rm eq}}{[{\rm A}]_{\rm eq}}$$

That is, the equilibrium constant is simply the ratio of forward and backward rate constants.

Side or Concurrent Elementary Reactions

Sometimes the products observed are formed by the same reactants undergoing more than one reaction.

Le

deal

For example, α -D-glucose and β -D-glucose are formed in the solution from the aldehydic form of D-glucose following the different reactions.

Let us consider a reactions in which A is converted into B and C by two different reactions at the same time.

Rate of consumption of A in A ---- B conversion

$$\therefore -\left(\frac{d[A]}{dt}\right)_1 = k_1[A] = \text{Rate of reaction}$$

Similarly, rate of consumption of A in $A \rightarrow C$ conversion

$$\therefore -\left(\frac{d[A]}{dt}\right)_2 = k_2[A] = \text{Rate of reaction}$$

Therefore, the overall net rate of consumption of A or net rate

reaction =
$$\frac{-d[A]}{dt} = -\left(\frac{d[A]}{dt}\right)_1 + \left(\frac{-d[A]}{dt}\right)_2$$

$$\frac{-d [A]}{dt} = k_1[A] + k_2[A]$$

$$= [k_1 + k_2] [A]$$

$$= k_{\text{overall}} [A] \qquad ...(i)$$

where $k_{\text{overall}} = k_1 + k_2$

Integrating Eq. (i), we get

$$[A] = [A]_0 e^{-(k1 + k2)t}$$

Also, from the rate equation:

$$\frac{d[\mathbf{B}]}{dt} = +k_1[\mathbf{A}] \text{ and } \frac{d[\mathbf{C}]}{dt} = +k_2[\mathbf{A}]$$

Substituting the value of [A] (t) in the differential equation for [B] and [C] and integrating, we get

[B] = [B]₀ +
$$\int_{0}^{t} k_{1} [A]_{0} e^{-(k_{1} + k_{2})t} dt$$

= [B]₀ $\frac{k_{1} [A]}{(k_{1} + k_{2})} (1 - e^{-(k_{1} + k_{2})t})$

and [C] =
$$[C]_0 + \int_0^t k_2 [A]_0 e^{-(k_1 + k_2)t} dt$$

= $[C]_0 \frac{k_1 [A]}{(k_1 + k_2)} (1 - e^{-(k_1 + k_2)t})$

Also, if
$$[B]_0 = [C]_0 = 0$$
, we get: $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

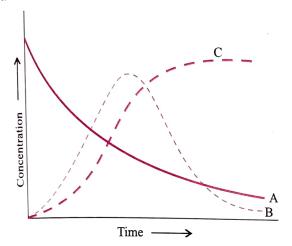
Consecutive or Sequential Reactions

In many reactions, the reactants form a stable intermediate compound before they are finally converted into the products. For example, reactant A is first converted to intermediate B which in turn is converted to product C as:

$$A \xrightarrow{k_1} B \text{ (Step I)}$$

$$B \xrightarrow{k_2} C \text{ (Step II)}$$
...(i)

Let the initial concentration of A be [A]₀ and let after time t, the concentration of A, B, and C be [A], [B], and [C], respectively. It is clear from Eq. (i) that B is produced by step I and consumed by It is clear from Eq. (i) that B is produced by step I and consumed by It In these reactions, each stage will have its own rate and rate constant. When we start with pure A, its concentration will decrease with time. The concentration of the intermediate will first increase with time. The concentration of the intermediate will first increase and it accumulates and reaches a maximum value. After attaining maximum value, it decreases and decays to zero concentration and is converted to the final product. The concentration of the product C will always increase. These results are shown in Fig. 4.3.



.3 Concentration profile of reactants (A), intermediate (B), and products (C) as a function of time

The differential rate expressions are:

$$\frac{d[A]}{dt} = -k_1[A] \qquad ...(ii)$$

$$\frac{d[B]}{dt} = + k_1[A] - k_2[B] \qquad ...(iii)$$

$$\frac{d[C]}{dt} = +k_2[B] \qquad ...(iv)$$

On solving the above differential equations, we get

[A] = [A]₀
$$e^{-k1t}$$
 ...(v)

[B] = [A]₀
$$\frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$
 ...(vi)

[C] = [A]₀
$$\left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right)$$
 ...(viii)

[B] is maximum, when $\frac{d[B]}{dt} = 0$

s. F^{or}

Differentiating Eq. (vi) with respect to t, we get

$$t_{\text{max}} = \frac{1}{k_2 - k_1} \ln \left(\frac{k_2}{k_1} \right) = \frac{2.303}{k_2 - k_1} \log \left(\frac{k_2}{k_1} \right)$$

Thus, at
$$t = \frac{2.303}{k_2 - k_1} \log \left(\frac{k_2}{k_1}\right)$$
, [B] is maximum

Two important conclusions can be derived from the study of above elementary process which forms the basis for deriving the differential rate laws of complex reaction. These are (a) the slowest elementary process (i.e., the process having reaction and (b) the steady state approximation which states that the reactive intermediates are present at constant concentrations.

4.6 MECHANISM OF A REACTION

In case of complex reactions, i.e., reactions involving a large number of molecules of the reactants according to the balanced equation, the chances for all the molecules to come closer and collide simultaneously are rare. Hence, in such cases, the reactions are supposed to take place in a number of steps.

A series of step reactions or elementary reactions proposed to account for the overall reaction is called the mechanism of the reaction.

The step reactions are usually written based upon experimental evidences, e.g., the detection of the presence of some short-lived intermediate (mostly atoms or unstable compounds), etc. However, a complete certainty of the steps is rarely possible.

A rate-determining step (i.e., slowest step) involves the molecule on which the rate of reaction actually depends as observed experimentally and written in the rate law equation. Moreover, the sum of step reactions must satisfy the overall stoichiometry of the reaction.

Following examples illustrate the concept of mechanism more clearly:

a. Decomposition of H_2O_2 which is catalyzed by $I^{\scriptsize \ominus}$ ion in basic medium

$$2H_2O_2 \xrightarrow{I^{\odot}} 2H_2O + O_2$$

The rate equation for this reaction is found to be

Rate =
$$\frac{-d [\mathrm{H_2O_2}]}{dt} = k [\mathrm{H_2O_2}] [\mathrm{I}^{\Theta}]$$

This reaction is of first order with respect to both H_2O_2 and I^{\odot} . Evidences suggest that this reaction takes place in two steps.

i.
$$H_2O_2 + I^{\odot} \longrightarrow H_2O + IO^{\odot}$$
 (slow)

ii.
$$\frac{H_2O_2 + IO^{\odot} \longrightarrow H_2O + I^{\odot} + O_2}{2H_2O_2 \longrightarrow 2H_2O + O_2 \text{ (net reaction)}}$$
 (fast)

Both the steps are bimolecular elementary reactions. Species IO[©] is called as an intermediate since it is formed during the course of the reaction but not in the overall balanced equation. The first step, being slow, is the rate-determining step. Thus, the rate of formation of intermediate will determine the rate of this reaction.

All the steps taken together give the mechanism of the reaction. The sum of the equations for the separate consecutive steps give the overall reaction.

b. Reaction between NO₂ and CO

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Rate =
$$k[NO_2]^2$$

The experimental observations reveal that the rate of reaction is proportional to the square of the concentration of nitrogen peroxide. This indicates that the rate- determining step in the mechanism of this reaction must be independent of the concentration of CO. Keeping this in mind, a mechanism of the reaction may be suggested as:

Although the above reaction proceeds through two steps but the rate of overall reaction is determined by the first step which is the slower of the two steps. Accordingly, the experimentally observed rate of the reaction is given by the expression: Rate = $k[NO_2]^2$

4.6.1 APPLICATIONS OF MECHANISM OF REACTION

The most important application of studying the order of a reaction is to use it in establishing the mechanism of the reaction.

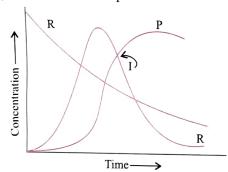
a. Reaction involving two first order consecutive steps

In such reactions, a reaction takes place in two steps both of which are first order.

$$R \xrightarrow{k_1} I(I)$$

$$I \xrightarrow{k_2} P(II)$$

Now intermediate I is produced by step I and consumed by step II. The intermediate I accumulates and reaches a maximum after which it decays to zero concentration and is converted into the final product as shown in Fig. 4.4.



Concentration profiles of R (reactant), I (intermediate), and P (product) as a function of time

b. Reactions involving slow steps

If a reaction takes place by a sequence of steps and one of the steps is slow, then the rate-determining step is the slow step. The rate of this step may be slow either due to low value of the rate constant or a low concentration of one or more of the reacting species in that elementary reaction. For example, in the reaction

$$R \xrightarrow{k_1} I \qquad I \xrightarrow{k_2} P$$

if $k_1 \ll k_2$, then I is converted into the product as soon as it is formed and we can say

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

This can be understood easily by the following analogy. Suppose a message is to be sent from London to New Delhi. In the first case, a person writes a letter and sends it by post and then the postman delivers this letter to the second person. The two steps can be written as:

Message with sender — By post — Message in New Delhi

Deliver time Message with Message with postman receiver

It is obvious that the first step is so slow that nearly all the time is taken by it and hence it is rate determining. In the second case, the sender in London sends the message by telegram which is then delivered by the postman in New Delhi. We can now write the two steps:

In this case, the first step is very fast and takes only a few seconds and the rate-determining step is the time taken by the postman to deliver the massage.

In the reaction: $3\text{ClO}^{\odot} \longrightarrow \text{CIO}_3^{\odot} + 2\text{Cl}^{\odot}$, various steps

$$ClO^{\ominus} + ClO^{\ominus} \longrightarrow ClO_2^{\ominus} + Cl^{\ominus}$$
 (slow step)
(rate-determining step)

$${\rm ClO_2}^{\ominus} + {\rm ClO}^{\ominus} \longrightarrow {\rm ClO_3}^{\ominus} + {\rm Cl}^{\ominus} \qquad \qquad ({\rm fast \ step})$$

Rate = k_1 [ClO $^{\odot}$]²

c. Reactions for which steady state hypothesis is valid

A reaction may take place in a number of steps and may have several intermediates. In the steady state hypothesis, we assume that the intermediates are so reactive that after a brief initial period (called induction period) their concentrations rise from zero to a small value and remain constant for most of the duration of the reaction, i.e., we can assume that change in the concentration with time for these reactive intermediates is zero. This assumption is very helpful for deriving the rate expression for complex reactions.

d. Reactions involving intermediates in equilibrium with the reactants

i. In some reactions specially involving H[⊕] and OH, there is an equilibrium established between the reactants as both forward and reverse reactions have very large rate constants. The intermediate thus formed reacts so slowly that the equilibrium concentration of the intermediate is not disturbed much. For example, the displacement of C₂H₅O[©] from o-hydroxy-amino ethyl benzoate is catalyzed by OH. The following mechanism has been suggested:

$$\begin{array}{c}
 & H \\
 & H \\
 & N \\
 & O \\$$

$$[I] = \frac{k_1 \text{ [Ester] [OH]}}{k_2}$$

Rate of reaction =
$$k_3$$
 [I] = $\frac{k_3 k_1}{k_2}$ [Ester] [OH]

$$= k_0$$
 [Ester] [OH]

This is a second order reaction, but the overall rate constant involves all the three rate constants, or we have $k_0 = \frac{k_3 k_1}{k_2}$

ILLUSTRATION 4.38

Mechanism of the reaction is:

$$A_2 \stackrel{k}{\rightleftharpoons} 2A$$

$$A+B_2 \xrightarrow{k_1} C+B$$

$$B+A_2 \xrightarrow{k_2} C+A$$

What is (a)
$$\frac{-d[A_2]}{dt}$$
 (b) $\frac{-d[A]}{dt}$ (c) $\frac{d[B]}{dt}$ (d) $\frac{d[C]}{dt}$

Sol.

a.
$$\frac{-d[A_2]}{dt} = k[A_2] - 2k'[A]^2 + k_2[B][A_2]$$

b.
$$\frac{-d[A]}{dt} = 2k'[A]^2 - k[A_2] + k_1[A][B_2] - k_2[B][A_2]$$

c.
$$\frac{d[B]}{dt} = k_1[A][B_2] - k_2[B][A_2]$$

d.
$$\frac{d[C]}{dt} = k_1[A][B_2] + k_2[B][A_2]$$

ILLUSTRATION 4.39

Mechanism of the reaction is:

$$A \xrightarrow{k_1} B$$
, $2A \xrightarrow{k_2} C + D$

What is
$$\frac{-d[A]}{dt}$$
?

Sol.
$$\frac{-d[A]}{dt} = k_1[A] + 2k_2[A]^2$$

ILLUSTRATION 4.40

Mechanism of the reaction is:

What is
$$\frac{-d[A]}{dt}$$
?

Sol.
$$\frac{-d[A]}{dt} = k_1[A] + k_2[A] + k_3[A]$$

= [A] $(k_1 + k_2 + k_3)$

ILLUSTRATION 4.41

Mechanism of the reaction is:

$$A \stackrel{k_1}{\rightleftharpoons} B$$
 ...(i)

$$B + A \xrightarrow{k_3} C \qquad ...(ii)$$

What is (a)
$$\frac{-d[A]}{dt}$$
; (b) $\frac{d[B]}{dt}$; (c) $\frac{d[C]}{dt}$?

Sol.

a. Rate of disappearance of [A] = $\frac{-d[A]}{dt}$

From step (1) =
$$k_1[A] - k_2[B]$$

From step (2) =
$$k_3$$
[B] [A].

$$\therefore \frac{-d[A]}{dt} = k_1[A] - k_2[B] + k_3[B][A]$$

b.
$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[A][B]$$

c.
$$\frac{d[C]}{dt} = k_3[A][B]$$

ILLUSTRATION 4.42

Mechanism of the reaction is:

$$A_2 \stackrel{k_1}{\rightleftharpoons} 2A$$

$$A + B \xrightarrow{k_2} C$$

$$A_2 + C \xrightarrow{k} D + A$$

What is (a)
$$\frac{-d[A_2]}{dt}$$
; (b) $\frac{-d[A]}{dt}$; (c) $\frac{d[C]}{dt}$; (d) $\frac{d[D]}{dt}$?

Sol

 $A \xrightarrow{k_1} B$ k_2 C

a.
$$\frac{-d[A_2]}{dt} = k_1[A_2] - 2k_1[A]^2 + k[A_2][C]$$

b.
$$\frac{-d[A]}{dt} = 2k_1[A]^2 - k_1[A_2] + k_2[A][B] - k[A_2][C]$$

$$c \cdot \frac{d[C]}{dt} = k_2[A][B] - k[A_2][C]$$

d.
$$\frac{d[D]}{dt} = k[A_2][C]$$

ILLUSTRATION 4.43

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

If
$$\frac{-d[N_2O_5]}{dt} = k_1[N_2O_5]$$

$$\frac{d\left[NO_{2}\right]}{dt} = k_{2}[N_{2}O_{5}]$$

$$\frac{d\left[O_{2}\right]}{dt} = k_{3}[N_{2}O_{5}]$$

What is the relation between k_1 , k_2 , and k_3 ?

Sol.
$$\frac{-d \left[\text{N}_2 \text{O}_5 \right]}{2 dt} = \frac{d \left[\text{NO}_2 \right]}{4 dt} = \frac{d \left[\text{O}_2 \right]}{dt}$$

$$\frac{k_1[N_2O_5]}{2} = \frac{k_2[N_2O_5]}{4} = \frac{k_3[N_2O_5]}{1}$$

Multiply by 4, we get

$$2k_1 = k_2 = 4k_3$$

ILLUSTRATION 4.44

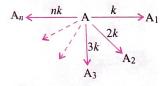
$$2SO_2 + O_2 \stackrel{k_1}{\rightleftharpoons} 2SO_3$$

What are the expressions for the rate law of the forward and backward reactions?

Sol. Rate of forward reaction, $R_f = k_1[SO_2]^2[O_2]$ Rate of backward reaction, $R_b = k_2[SO_3]^2$

ILLUSTRATION 4.45

Mechanism of the reaction is:



What is (a) $\frac{-d[A]}{dt}$; (b) $\frac{d[A_1]}{dt}$; (c) $\frac{d[A_n]}{dt}$; (d) $\frac{d[A_1]}{-d[A]}$

for same time?

Sol.

a.
$$\frac{-d[A]}{dt} = [k + 2k + 3k + \dots + nk][A]$$
$$= [1 + 2 + 3 + \dots + n][k][A]$$
$$= \frac{n(n+1)}{2}k[A]$$

b.
$$\frac{d[A_1]}{dt} = k[A]$$

c.
$$\frac{d[A_n]}{dt} = nk [A]$$

d.
$$\frac{d[A_1]}{-d[A]} = \frac{k[A]}{\frac{n(n+1)}{2}k[A]} = \frac{2}{n(n+1)}$$

ILLUSTRATION 4.46

The rate law for the decomposition of gaseous N_2O_5 ,

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$
 is observed to be:

$$r = \frac{-d [N_2O_5]}{dt} = k[N_2O_5]$$

A reaction mechanism which has been suggested to be consistent with this rate law is

$$N_2O_5(g) \xrightarrow{k_{eq}} NO_2(g) + NO_3(g)$$
 (fast equilibrium)

$$NO_2(g) + NO_3(g) \xrightarrow{k_1} NO_2(g) + NO(g) + O_2(g)$$
 (slow)

$$NO(g) + NO_3(g) \xrightarrow{k_2} 2NO_2(g)$$
 (fast)

Show that the mechanism is consistent with the observed rate law

Sol.
$$r = k_1[NO_2][NO_3]$$
 ...(i)

and from the fast equilibrium step,

$$k_{\text{eq}} = \frac{[\text{NO}_2][\text{NO}_3]}{[\text{N}_2\text{O}_5]}$$

Thus,
$$[NO_2][NO_3] = k[N_2O_5]$$
 ...(ii)

Using Eq. (ii) in Eq. (i), we get

$$r = k_1 k_{eq} [N_2 O_5] = k [N_2 O_5]$$
 where $k = k_1 k_{eq}$

This shows that the mechanism is consistent with the observed rate law.

ILLUSTRATION 4.47

The termolecular reaction

 $2NO(g) + H_2(g) \longrightarrow 2NOH(g)$ is found to be third order obeying the rate law $r = k[NO]^2 [H_2]$. Show that it is consistent with either of the following mechanisms:

a.
$$2NO(g) \stackrel{k_{eq}}{\rightleftharpoons} N_2O_2(g)$$
 (fast equilibrium)

$$N_2O_2(g) + H_2(g) \xrightarrow{k'} 2NOH(g)$$
 (slow)

b.
$$2NO(g) + H_2(g) \xrightarrow{k'_{eq}} NOH_2(g)$$
 (fast equilibrium)
 $NOH_2(g) + NO(g) \xrightarrow{k''} 2NOH(g)$ (slow)

Sol.

a. Since the slow step is the rate-determining step, Hence, $r = k' [N_2 O_2] [H_2]$

$$\Rightarrow r = k' \ k_{\text{eq}} [\text{NO}]^2 [\text{H}_2] = k[\text{NO}]^2 [\text{H}_2]$$
(where $k = k' k_{\text{eq}}$)

b. Proceeding as in (a) above, we have $r = k'' [NOH_2] [NO]$

and from the fast equilibrium step,

$$k_{\text{eq}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \text{ or } [\text{N}_2\text{O}_2] = k_{\text{eq}} [\text{NO}]^2$$

and from the fast equilibrium step,

$$k'_{\text{eq}} = \frac{[\text{NOH}_2]}{[\text{NO}][\text{H}_2]} \text{ or } [\text{NOH}]_2 = k'_{\text{eq}} [\text{NO}][\text{H}_2]$$

$$\Rightarrow r = k'' \ k'_{eq} [NO]^2 [H_2] = k [NO]^2 [H_2]$$
(where $k = k'' \ k'_{eq}$)

ILLUSTRATION 4.48

For and elementary reaction

 $2A \stackrel{k_1}{\rightleftharpoons} B$, the rate of disappearance of A is equal to

a.
$$\frac{2k_1}{k_2}[A]^2$$

b.
$$-2k_1[A]^2 + 2k_2[B]$$

c.
$$2k_1[A]^2 - 2k_2[B]$$

d.
$$(2k_1 - k_2)$$
 [A]

.: Rate of disappearance of A

$$= \frac{-d[A]}{dt} = 2k_1[A]^2 - 2k_2[B]$$

ILLUSTRATION 4.49

Consider the following reactions:

$$1. A+B \xrightarrow{k_1} C$$

II.
$$C+B \xrightarrow{k_2} D$$

Then $k_1[A][B] - k_{-1}[C] - k_2[C][B]$ is equal to

a.
$$\frac{-d[A]}{dt}$$

b.
$$\frac{-d [B]}{dt}$$

c.
$$\frac{d[C]}{dt}$$

d.
$$\frac{d[D]}{dt}$$

c.
$$A + B \stackrel{k_1}{\rightleftharpoons} C$$

Rate of C = k_1 [A] [B] $-k_{-1}$ [C]

$$C + B \xrightarrow{k_2} D$$

Rate of disappearance of $C = -k_2[C][B]$

⇒ Net rate of C

$$= k_1 [A] [B] - k_{-1} [C] - k_2 [C] [B]$$

$$= \frac{d [C]}{dt}$$

LLUSTRATION 4.50

The rate expression of some reactions are given below. Propose ² probable mechanism of each of the following reactions:

a.
$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$
;

Rate =
$$k [N_2O_5]$$

b.
$$2NO_2 + F_2 \longrightarrow 2NO_2F$$
; Rate = $k [NO_2] [F_2]$

Rate =
$$k$$
 [NO₂] [F₂]

Ka

a. Rate =
$$k [N_2O_5]$$

$$\begin{array}{ccc}
N_2O_5 & \xrightarrow{Slow} & NO_2 + NO_3 \\
NO_3 + N_2O_5 & \xrightarrow{Fast} & 3NO_2 + O_2 \\
\hline
2N_2O_5 & \longrightarrow 4NO_2 + O_2
\end{array}$$

b. Rate =
$$k [NO_2] [F_2]$$

$$NO_2 + F_2 \xrightarrow{Slow} NO_2F + F$$

$$F + NO_2 \xrightarrow{Fast} NO_2 F$$

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

ILLUSTRATION 4.51

In the following reaction:

$$2NO(g) + O_2(g) \xrightarrow{k'} 2NO_2(g),$$

What is the predicted rate law, if the mechanism is

$$NO + O_2 \stackrel{k_{eq}}{\longleftarrow} NO_3$$
 (fast)

$$NO_2 + NO \xrightarrow{k_1} NO_2 + NO_2$$
 (slow)

Sol. Rate law, according to the slowest step is:

$$r = k_1 [NO_3] [NO] \qquad ...(i)$$

First step is in equilibrium.

$$\therefore k_{eq} = \frac{[NO_3]}{[NO][O_2]}$$

$$\therefore [NO_3] = k_{eq} [NO] [O_2]$$

Substituting the value of [NO₃] in Eq. (i)

$$r = k_1 k_{eq} [NO] [O_2] [NO] = k' [NO]^2 [O_2]$$

ILLUSTRATION 4.52

A reaction is found to proceed in two steps as $A + B \longrightarrow E$ (slow); $A + E \longrightarrow C + D$ (fast). Write the law expression and overall balanced equation.

Sol.
$$A + B \longrightarrow E$$
 (slow)

$$A + E \longrightarrow C + D$$

(fast)

The overall reaction

$$2A + B \longrightarrow C + D$$

Since the slow step is the rate-determining step,

$$\therefore r = k [A] [B].$$

ILLUSTRATION 4.53

A chemical reaction proceeds as follows:

$$A + C \longrightarrow D + F$$
 (Slow)

$$F + B \longrightarrow G$$
 (Fast)

$$G + C \longrightarrow E$$
 (Fast)

Suggest rate law; overall under; units for rate constant; and overall reaction.

Sol.
$$A + C \longrightarrow D + F$$
 (Slow)

$$F + B \longrightarrow G$$
 (Fast)

$$G + C \longrightarrow E$$
 (Fast)

$$A + B + 2C \longrightarrow D + E$$
 (The overall reaction)

Slowest step is the rate-determinig step.

$$\therefore r = k [A] [C]$$

Order of reaction = 1 + 1 = 2

Units for k for second order = $mol^{-1} L s^{-1}$

ILLUSTRATION 4.54

For the chemical reaction:

$$5Br^{\odot} + BrO_3^{\odot} + 6H^{\oplus} \longrightarrow 3Br_2 + 3H_2O$$

Rate =
$$k [Br^{\odot}] [BrO_3^{\odot}] [H^{\oplus}]^2$$

What is the molecularity and order of reaction with respect to [Br[⊙]]?

Sol.
$$5Br^{\odot} + BrO_3^{\odot} + 6H^{\oplus} \longrightarrow 3Br_2 + 3H_2O$$

Molecularity w.r.t. $Br^{\Theta} = 5$

Rate = $k[Br^{\ominus}][BrO_3^{\ominus}][H^{\oplus}]^2$

Order w.r.t. $[Br^{\Theta}] = 1$

ILLUSTRATION 4.55

For the chemical reaction:

$$I^{\scriptsize \bigcirc} + OCl^{\scriptsize \bigcirc} \longrightarrow Cl^{\scriptsize \bigcirc} + OI^{\scriptsize \bigcirc}$$

Rate =
$$\frac{k [OCI^{\odot}][I^{\odot}]}{[OH]}$$

- a. What is the order and molecularity of the reaction?
- b. In the above reaction, what are the molecularity and order with respect to [OH]?

Sol.

a. Rate =
$$\frac{k [OCl^{\odot}][I^{\odot}]}{[OH]}$$

Order of reaction = 1 + 1 - 1 = 1

Molecularity of reaction = 1 + 1 = 2

b. Molecularity w.r.t.
$$[OH] = 0$$

Order w.r.t. [OH] = -1

ILLUSTRATION 4.56

The chemical reaction $2O_3 \xrightarrow{k_1} 3O_2$ proceeds as follows:

$$O_3 \stackrel{k_{eq}}{\smile} O_2 + O$$
 (fast)

$$O + O_3 \xrightarrow{k} 2O_2$$
 (slow)

What should be the rate law expression?

Sol.
$$2O_3 \xrightarrow{k_1} 3O_2$$

Mechanism:

$$O_3 \stackrel{k_{eq}}{\longleftarrow} O_2 + O$$
 (fast)

$$\begin{array}{ccc}
O + O_3 & \xrightarrow{k} & 2O_2 \\
\text{Retark of d} & & & & & \\
\end{array}$$
(slow)

Rate of the reaction from the slow step is

$$r = k \text{ [O] [O_3]}$$
Foot step ...(i)

Fast step is in equilibrium, the concentration of [O] is calculated from this step

$$k_{\text{eq}} = \frac{[O_2][O]}{[O_3]}$$
 $\therefore [O] = \frac{k_{\text{eq}} \cdot [O_3]}{[O_2]}$

Substitute the value of [O] in Eq. (i)

$$r = \frac{k \cdot k_{\text{eq}} \cdot [O_3][O_3]}{O_2} = \frac{k_1 [O_3]^2}{[O_2]} = k_1 [O_3]^2 [O_2]^{-1}$$

ILLUSTRATION 4.57

Mechanism of a reaction is given below:

chanism of a reaction
$$= 2$$

 $X_2 \longrightarrow 2X, k_1 = 10^5 \text{ s}^{-1} \text{ (forward)}$

$$k_2 = 10^5 \text{ s}^{-1} \text{ (backward)}$$

$$k_2 = 10^3 \text{ s}$$
 (backward)
 $X + Z \longrightarrow XZ$, $k_3 = 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

Write the rate law and calculate the order of overall reaction

Sol.
$$X_2 \rightleftharpoons 2X, k_1 = 10^5 = k_2$$

(This is equilibrium step)

$$X + Z \longrightarrow XZ$$
, $k_3 = 10^{-4}$ (Value of k_3 is very less as compared to k_1 and k_2).

So it is slow step and is the rate-determining step

$$\therefore$$
 Rate = k_3 [X] [Z]

$$Rate = \kappa_3 \left[\Lambda_J \left[\Sigma_J \right] \right] \qquad \dots (i)$$

$$k_{\rm eq} = \frac{k_2}{k_1} = \frac{10^5}{10^5} = 1$$

$$\therefore 1 = \frac{[X]^2}{[X_2]}, \qquad [X] = [X_2]^{1/2}$$

Substitute the value of [X] in Eq. (i)

Rate =
$$k_3 [X_2]^{1/2} [Z]$$

$$\therefore$$
 Order of reaction = $\frac{1}{2} + 1 = \frac{3}{2}$

ILLUSTRATION 4.58

For the reaction

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH$$
, the rate of formation of Fe³⁺ is given by

Rate = k [Fe²⁺] [H₂O₂]. Suggest a mechanism for the reaction and indicate a probable rate-determining step.

Sol. The reaction is:

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH$$

Rate =
$$k[Fe^{2+}][H_2O_2]$$

The mechanism is:

$$Fe^{2+} + H_2O_2 \xrightarrow{Slow} Fe^{3+} + OH + OH$$

$$Fe^{2+} + OH \xrightarrow{Fast} Fe^{3+} + OH$$

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH$$

ILLUSTRATION 4.59

Deduce the rate law for the conversion of H₂ and I₂ to HI at 440°C corresponding to the following proposed mechanism:

Step I:
$$I_2 \rightleftharpoons 2I$$
 (fast) (k_1)

Step II:
$$I + H_2 \rightleftharpoons IH_2$$
 (fast) (k_2)

Step III:
$$IH_2 + I \longrightarrow 2HI$$
 (slow) (k)

$$\begin{array}{ccc}
\mathbf{1.} & \stackrel{1}{\cancel{}} & \stackrel{2}{\cancel{}} & & \\
\mathbf{2.} & & & & & & \\
\mathbf{1} + \mathbf{H}_2 & \xrightarrow{} & & & & \\
\end{array}$$
(fast) (k_2)

3.
$$IH_2 + I \xrightarrow{k} 2HI$$
 (slow) (k)

Steps (I) and (II) are fast and reversible.

From step (1),
$$k_1 = \frac{[1]^2}{[I_2]}$$

$$\therefore [I]^2 = k_1 [I_2]$$

$$[1] = k_1^{1/2} [1_2]^{1/2} \qquad ...(ii)$$

Similarly, from step (II),

$$k_2 = \frac{[\mathbb{IH}_2]}{[\mathbb{I}][\mathbb{H}_2]}$$

$$[\mathbb{IH}_2] = k_2 [\mathbb{I}] [\mathbb{H}_2] \qquad ...(iii)$$

Substitute Eqs. (ii) and (iii) in (i),

Rate =
$$k_2 k[I] [H_2] k_1^{\frac{1}{2}} [I_2]^{\frac{1}{2}}$$

= $k k_2 k_1^{\frac{1}{2}} k_1^{\frac{1}{2}} [I_2]^{\frac{1}{2}} [H_2] [I_2]^{\frac{1}{2}}$
= $k k_2 k_1 [I_2]^{\frac{1}{2}} [H_2] [I_2]^{\frac{1}{2}}$
= $k k_2 k_1 [I_2] [H_2]$
= $k' [I_2] [H_2]$
= $k' [I_2] [H_2]$

ILLUSTRATION 4.60

For the overall reaction between A and B to yield C and D, two mechanisms are proposed:

$$A + B \longrightarrow AB^* \longrightarrow C + D$$
 $k_1' = 1 \times 10^{-5} M^{-1} s^{-1}$

$$k_1' = 1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$$

$$\Pi \quad A \longrightarrow A^* \longrightarrow E,$$

$$k_1 = 1 \times 10^{-4} \text{ s}^{-1}$$

$$E+B\longrightarrow C+D$$
,

$$k_2 = 1 \times 10 \text{ s}^{-1}$$

- a. Write the rate law expression for each mechanism when initial concentration of each is 0.1 M.
- b. At that concentration of A and/or B, will the inherent rates

Sol. Rate_I =
$$k_1'$$
 [A][B] = 1 × 10⁻⁵ (0.1) (0.1) = 1 × 10⁻⁷ M s⁻¹
Rate_{II} = k_1 [A] = 1 × 10⁻⁴ × 0.1

$$= 1 \times 10^{-5} \text{ M s}^{-1}$$

(Its second step is fast and first step is slow as evident from k_1 and k_2 values)

If rates are equal, then $k_1'[A][B] = k_t[A]$

$$\therefore k_1'[A] = k_t$$

: [B] =
$$\frac{k_1}{k_1'} = \frac{1 \times 10^{-4} \,\text{s}^{-1}}{1 \times 10^{-5} \,\text{M}^{-1} \,\text{s}^{-1}} = 10 \,\text{M}$$

CONCEPT APPLICATION EXERCISE 4.2

1. The gaseous decomposition of ozone

$$2O_3 \longrightarrow 3O_2$$

obeys the rate law
$$r = \frac{-d [O_3]}{dt} = \frac{k[O_3]^2}{[O_2]}$$

Show that the following mechanism is consistent with the above rate law:

$$O_3 \stackrel{k_{eq}}{\longrightarrow} O_2 + O$$
 (fast)

$$O + O_3 \xrightarrow{k_1} 2O_2$$
 (slow)

2. For the formation of phosgene from CO(g) and chlorine, $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$

the experimentally determined rate equation is

$$\frac{d[COCl_2]}{dt} = k[CO] [Cl_2]^{3/2}$$

Is the following mechanism consistent with the rate equation?

a.
$$Cl_2 \Longrightarrow 2Cl$$
 (fast)

b.
$$Cl + CO \rightleftharpoons COCl$$
 (fast)

c.
$$COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$$
 (slow)

3. Rate law for ozone layer depletion is

$$\frac{d[\mathcal{O}_3]}{dt} = \frac{k[\mathcal{O}_3]^2}{[\mathcal{O}_2]}$$

Give the probable mechanism of reaction?

4. In hypothetical reaction, $A_2 + B_2 \longrightarrow 2AB$ follows the mechanism as given below:

$$A_2 \rightleftharpoons A + A$$
 (fast reaction)

$$A + B_2 \longrightarrow AB + B$$
 (slow reaction)

$$A + B \longrightarrow AB$$
 (fast reaction)

Give the rate law and order of reaction.

- 5. What is meant by an "accepted mechanism"? Is there any such thing as a proved mechanism?
- **6.** If a rate law has the form: Rate = $k[A][B]^{3/2}$, can the reaction be an elementary process? Explain.
- 7. During the initial stages of the reaction:

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$
, the rate law is:

$$\frac{d[HBr]}{dt} = k[H_2][Br_2]^{1/2}$$

Is the above reaction an elementary reaction?

8. Write the equation which represents the rate law for each of the following elementary processes:

$$A + B \longrightarrow C + D$$

$$2A \longrightarrow E + F$$

9. For the hydroylsis of methyl formate, HCOOCH₃, in acid

Rate = $k [HCOOCH_3] [H^{\oplus}]$

The balanced equation is:

 $HCOOCH_3 + H_2O \longrightarrow CH_3OH + HCOOH$ why does $[H^{\oplus}]$ appear in the rate law, when it does not appear in the balanced equation.

10. Explain why a catalyst which could accelerate the reactions given below would be of great value.

$$2NO_2 + 4CO \longrightarrow N_2 + 4CO_2$$
$$2NO + 2CO \longrightarrow N_2 + 2CO_2$$

ANSWERS

(1, 2, 3) factual 4. O.R. = 3/2(5 to 10) factual

4.7 INTEGRATED RATE EQUATION OF DIFFERENT ORDER REACTIONS

We have already discussed that for a general reaction:

$$aA + bB \longrightarrow cC + dD$$

Rate =
$$\frac{-d[R]}{dt} = k[A]^{\alpha}[B]^{\beta}$$

This form of the equation is called differential rate equation. This form relates the rate of change of concentration with time or instantaneous rate. It is not always convenient to determine the instantaneous rate as it is measured by the determination of the slope of the tangent at point t in the concentration versus time curve (see Fig. 4.5). This makes it difficult to determine the rate law and hence the determination of the order of the reaction. In order to avoid this difficulty, we can integrate the rate equation and obtain integrated rate equation that gives a relation between directly measured experimental quantities, i.e., concentrations at different times. The integrated rate equations are different for reactions of different orders.

4.7.1 ZERO ORDER REACTIONS

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

For the reaction

 $A \longrightarrow products$

to be of zero order,

Rate =
$$\frac{-d[A]}{dt} = k[A]^0 = k$$

or
$$d[A] = -k dt$$

Integrating both sides, we get

[A] =
$$-kt + c$$
 ...(i), where c is a constant of integration

At
$$t = 0$$
, $[A] = [A]_0$

$$\therefore [A]_0 = c$$

Substituting this value of I in Eq. (i), we get

$$[A] = -kt + [A]_0 \qquad \qquad \cdots (ii)$$

or
$$kt = [A]_0 - [A]$$

or
$$k = \frac{1}{t} \{ [A]_0 - [A] \}$$
 ...(iii)

This is the expression for the rate constant for reactions of zero order.

Characteristics of Zero Order Reactions

a. Any reaction of zero order must obey Eq. (ii)

$$[A] = [A]_0 - kt$$

This shows that the concentration of reactant decreases linearly with time, as it is an equation of a straight line (y = mx + c), the plot of [A] versus t will be straight line with slope = -k and intercept on the concentration axis = $[A]_0$ as shown in Fig. 4.5.

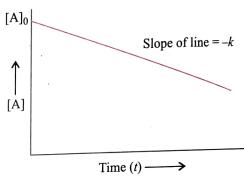


Fig. 4.5 Plot of [A] versus t for a reaction of zero order

Also, as the rate is independent of concentration, the plot of rate versus concentration will be a straight line parallel to the concentration axis (Fig. 4.6).

Note: The rate of reaction remains constant throughout the course of reaction.

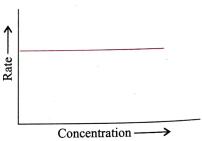


Fig. 4.6 Plot of rate versus concentrations for the reaction of zero order

b. Half life period: The time required to reduce the initial concentration of the reactant to half of its initial values is called half life time or half life period and is denoted by $t_{1/2}$. When $[A] = [A]_0/2$, $t = t_{1/2}$, substituting these values in Eq. (iii), we get

$$t_{1/2} = \frac{1}{k} \{ [A]_0 - [A]_0 / 2 \} = \frac{[A]_0}{2k}$$

i.e.,
$$t_{1/2} = \frac{[A]_0}{2k}$$
 or $t_{1/2} \propto [A]_0$.

Thus, the half-life period of zero order reaction is directly Thus, and initial concentration, i.e., $t_{1/2} \propto [A]_0$. p_{lore} , a plot of $t_{1/2}$ versus [A]₀ will be a straight line passing through the origin and slope = $\frac{1}{2}k$ (Fig. 4.7).

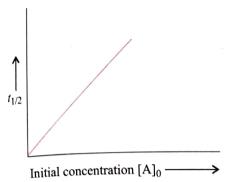


Fig. 4.7 Plot of $t_{1/2}$ versus [A]₀

c. Unit of rate constant (k): From Eq. (iii),

$$k = \frac{\text{Molar concentration}}{\text{time}} = \frac{\text{mol } L^{-1}}{\text{time}} = \text{mol } L^{-1} t^{-1}$$

Note: The units of rate and rate constant for zero order reactions

Zero order reactions generally take place in a heterogeneous system and some photochemical reactions are also zero order reactions. Such reactions are not common.

- d. Some examples of zero order reactions are as follows:
 - i. Photochemical reaction between hydrogen and chlorine:

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

This photochemical reaction is a zero order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. The rate of reaction is studied by noting the rate at which water rises in the vessel due to the dissolution of HCl formed. The rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2 , i.e., the concentration of the gases per unit volume in the gaseous phase will not change with time, although the quantities will change.

Note: In zero order reaction, it is the amount of reactant that changes and not the concentration.

For example:

For example:

$$H_{2} + Cl_{2} \longrightarrow 2HCl$$
Initial moles, $t = 0$

$$Final moles, $t = t$

$$At t = 0;$$

$$[H_{2}] = \frac{a}{V}$$

$$[Cl_{2}] = \frac{b}{V}$$

$$[Cl_{2}] = \frac{(b - x)}{V_{1}}$$$$

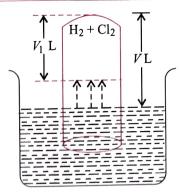


Fig. 4.8 Reaction between H2(g) and Cl2(g)

The HCl formed is dissolved in water and rises up in tube making the new volume V_1 , available for H_2 and Cl₂ left at any time, t.

Thus,
$$\frac{a}{V} = \frac{(a-x)}{V_1}$$
; $\frac{b}{V} = \frac{(b-x)}{V_1}$

ii. Decomposition of N₂O on hot platinum surface:

$$N_2O \longrightarrow N_2 + \frac{1}{2}O_2$$

Rate $\propto [N_2O]^0 = k[N_2O]^0 = k$

or
$$\frac{-d[N_2O]}{dt} = k$$

iii. Decomposition of NH₃ in the presence of molybdenum or tungsten is a zero order reaction:

$$2NH_3 \xrightarrow{[Mo]} N_2 + 3H_2$$

In such a system, the reactant is adsorbed on the surface of a solid catalyst (where it is converted into products). The fraction of the surface of the catalyst covered by the reactant is proportional to its concentration at low values and the rate of the reaction is first order. However, after certain concentration limit of the reactant, the surface of the catalyst is fully covered and any further increase of concentration of the reactant does not change the situation and the reaction rate becomes independent of concentration and the reaction becomes zero order. Thus, the decomposition of NH3 on finely divided catalyst surface is first order when the pressure of NH, in the system is low. At higher concentration when surface of the catalyst is fully covered with the layer of NH, molecules, the reaction becomes zero order. In general, the rate of reaction is given by the equation:

rate =
$$\frac{k_1[NH_3]}{1 + k_2[NH_3]}$$
, $\begin{bmatrix} k_1 \text{ and } k_2 \text{ are constants,} \\ \text{when } [NH_3] \text{ is very low.} \\ k_2[NH_3] \text{ can be neglect compared to unity.} \end{bmatrix}$

 \therefore At very low [NH₃]: rate = k_1 [NH₃] and the reaction is first order w.r.t. [NH₃].

At higher $[NH_3]$, neglect unity compared to $k_2[NH_3]$, we have

rate =
$$\frac{k_1[NH_3]}{k_2[NH_3]} = \frac{k_1}{k_2} = k$$

(i.e., rate is constant, a characteristic of zero order reaction

- iv. Decomposition of HI on the gold surface.
- v. Iodination of acetone in the presence of H^{\oplus} ions:

CH₃COCH₃ + I₂
$$\xrightarrow{\mathbb{H}^{\oplus}}$$
 ICH₂COCH₃ + HI

The rate equation of this reaction does not include $[I_2]$ factor, i.e.,

$$-\frac{dx}{dt} = k[CH_3COCH_3][H^{\oplus}]$$

vi. If either of the reactants is taken in excess, then also zero order reactions occur since in these the amount or concentration change is supposed to be negligible at any time.

Although reactions which have an overall order of zero are rare, it is not unusual to find the reaction in which the order of reaction with respect to one of the reactant is zero, e.g., enzyme-catalyzed reactions:

Rate =
$$k$$
[Enzyme]¹ [Substrate]⁰

Since the concentration of the substrate is in excess and that of enzyme is small.

4.7.2 FIRST ORDER REACTIONS

A reaction is said to be of first order if its rate is determined by the change of one concentration term only.

Consider the reaction:

$$A \longrightarrow products$$

Let a be the concentration of A at the start and after time t, the concentration becomes (a-x), i.e., x has been changed into products. The rate of reaction after time t is given by the expression.

$$\frac{dx}{dt} = k(a - x) \qquad \dots (i)$$

or
$$\frac{dx}{(a-x)} = k dt$$

Upon integration of above equation,

$$\int \frac{dx}{(a-x)} = k \int dt$$
$$-\ln(a-x) = kt + c$$

...(ii)

where c is the integration constant.

When
$$t = 0$$
, $x = 0$

$$c = -\ln a$$

Putting the value of c in Eq. (ii), we get

$$-\ln(a-x) = kt - \ln a$$

or
$$\ln a - \ln(a - x) = kt$$

or
$$\ln \frac{a}{(a-x)} = kt$$

or
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$
 or $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$...(iii)

This is known as the kinetic equation for a reaction of the first order.

Equation (iii) can be written in the exponential form as

$$\frac{[A]_0}{[A]} = e^{kt}$$

or
$$\frac{[A]}{[A]_0} = e^{-kt}$$

or
$$[A] = [A]_0 e^{-kt} \qquad \dots (iv)$$

Characteristics of First Order Reactions

a. Any reaction of the first order must obey Eq. (iii)

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \text{ or } k = \frac{2.303}{t} \log \left(\frac{a}{a-x}\right)$$

It can also be written as

$$\log [A] = \frac{-kt}{2.303} + \log[A]_0 \qquad ...(7)$$

This is the equation of a straight line (y = mx + c)

Thus, if log[A] or log(a-x) values are plotted against time t, the graph obtained should be a straight line. The intercept on y-axis would be $log[A]_0$ and the slope of the line would

be equal to
$$\left(\frac{-k}{2.303}\right)$$
, i.e., slope = $\frac{-k}{2.303}$ (Fig. 4.9).

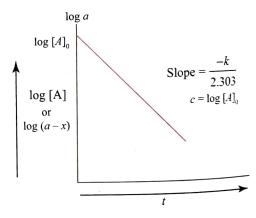


Fig. 4.9 Plot of log [A] vs time (t)

Thus, if we plot $\log \frac{[A]_0}{[A]}$ versus t, a straight line graph will be obtained with slope = k/2.303 as shown in Fig. 4.10.

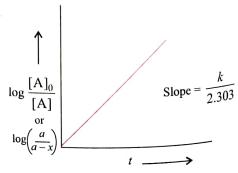


Fig. 4.10 Plot of $log([A]_0/[A])$ vs time (t)

$$\int_{x=0.5a}^{101 \text{ hds}} \int_{x=0.5a}^{101 \text{$$

or
$$t_{1/2} = \frac{0.693}{k}$$

Thus, $t_{1/2}$ is independent of initial concentration a.

The time t in which the initial concentration becomes half is termed as half life period. Half life period of a first order reaction is independent of the initial concentration of the

i. General expression for the time taken for *n*th fraction of a reaction of first order to complete:

Putting $x = \frac{a}{n}$ and $t = t_{1/n}$ in the first order equation

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$
, we get

$$t_{1/n} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{n}} = \frac{2.303}{k} \log \frac{1}{1 - 1/n}$$

or
$$t_{1/n} = \frac{2.303}{k} \log \frac{n}{n-1}$$

Thus, the time taken for any fraction of the first order reaction to complete is independent of the initial concentration.

ii. General expression for the time taken for the reactant to reduce to the *n*th fraction:

Here,
$$(a-x) = \frac{a}{n}$$

$$\therefore t = \frac{2.303}{t} \log \frac{a}{a/n}$$

or
$$t = \frac{2.303}{t} \log n$$

iii. Amount of substance left after n half lives: In general, substance left after n half lives

$$\frac{A_0}{2^n}$$
 or $\left(\frac{1}{2}\right)^n [A_0]$ and $n = \frac{\text{Total time}}{t_{1/2}}$

- The amount left in one half = $\frac{A_0}{2}$
- The amount left in two halves = $\frac{A_0}{(2)^2} = \frac{A_0}{4}$
- The amount left in three halves = $\frac{A_0}{(2)^3} = \frac{A_0}{8}$
- c. Unit of rate constant (k): Since the rate constant is independent of concentration and depends inversely on the time, the unit of k will be time⁻¹, i.e., s^{-1} or h^{-1} .
- d. Average life (λ) = $\frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.443t_{1/2}$

The time in which 63.2% substance undergo decay is called average life.

e. i. Relation between $t_{1/2}$ and $t_{x\%}$ (amount decomposed):

$$t_{x\%\text{(decomposed)}} = \frac{2.3}{k} \log \left(\frac{100}{100 - x} \right)$$
 ...(i)

$$t_{1/2} = \frac{0.69}{k} = \frac{0.3 \times 2.3}{k}$$
 ...(ii)

Divide Eq. (ii) by Eq. (i),

$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log\left(\frac{100}{100 - x}\right)}$$

ii. Similarly, relation between $t_{x\%}$ and $t_{y\%}$ (amount decomposed):

$$\frac{t_{x\%}}{t_{y\%}} = \frac{\log\left(\frac{100}{100 - x}\right)}{\log\left(\frac{100}{100 - y}\right)}$$

where x% and y% are the percentages of substance decomposed.

iii. Relation between $t_{1/2}$ and $t_{r\%}$ (amount left):

$$\frac{t_{1/2}}{t_{x\%(\text{left})}} = \frac{0.3}{\log\left(\frac{100}{x}\right)}$$

iv. Relation between $t_{r\%}$ and $t_{v\%}$ (amount left):

$$\left(\frac{t_{x\%}}{t_{y\%}}\right)_{\text{left}} = \frac{\log\left(\frac{100}{x}\right)}{\log\left(\frac{100}{y}\right)}$$

f. $t_{1/2} = \frac{0.693}{L}$ for first order reaction

and
$$t_{3/4} = 2t_{1/2}$$
 or $t_{75\%} = 2t_{1/2}$, $t_{87.5\%} = 3t_{1/2}$, $t_{25\%} = 0.4t_{1/2}$
and similarly $t_{99.9\%} = 10t_{1/2}$, $t_{96.87\%} = 5t_{1/2}$ and $t_{93.75\%} = 2t_{72\%}$
= $4t_{1/2}$ since $t_{72\%} = 2t_{1/2}$

In general, for nth order reaction

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}} \propto [A]_0^{1-n}$$

g. Starting with two different concentrations a_1 and a_2 for the same reaction, the half lives $(t_{1/2})_1$ and $(t_{1/2})_2$ are determined.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

or
$$n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}$$

n is the order of reaction.

- h. Some common examples of first order reactions are:
 - i. Hydrogenation of ethene:

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

- Rate = $k[C_2H_4]$
- ii. Decomposition of nitrogen pentoxide (N₂O₅):

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

Rate = $k[N_2O_5]$

iii. Decomposition of ammonium nitrite in aqueous solution:

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Rate = $k [NH_4NO_2]$

iv. Decomposition of H_2O_2 in the presence of I^{\odot} ions:

$$H_2O_2 \xrightarrow{I^{\odot}} H_2O + \frac{1}{2}O_2(g)$$

Rate =
$$k[H_2O_2]$$

 All natural and artificial radioactive isotopes of unstable nuclei occur by first order kinetics.

vi. Hydrolysis of ester:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^{\oplus}} CH_3COOH + C_2H_5OH$$

Rate = k [Ester]

vii. Hydrolysis of conc sugar:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$$
(Glucose) (Fructose)

Rate =
$$k$$
 [Sugar]

viii. Hydrolysis of benzene diazonium chloride:

$$PhN = NCl + H_2O \longrightarrow PhOH + N_2 + HCl$$

$$Rate = k [PhN_2Cl]$$

ix. Decomposition of thionyl chloride:

$$SO_2Cl_2 \xrightarrow{\Delta} SO_2 + Cl_2$$

Rate = $k [SO_2 Cl_2]$

4.7.3 SECOND ORDER REACTIONS

A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms.

The kinetics of second order reactions are given as follows:

When concentrations of both reactants are equal or two molecules of the same reactant are involved in the change, i.e.,

 $A+B \longrightarrow Products$

or $2A \longrightarrow Products$

Case I: When either one reactant or two reactants with same concentration.

$$2A \longrightarrow \text{Products} \quad \text{or} \quad A + B \longrightarrow \text{Products}$$

$$At t = 0 \qquad a \qquad 0 \qquad a \qquad a \qquad 0$$

$$At t = t \qquad (a - x) \qquad x \qquad (a - x) (a - x) \qquad x$$

$$\frac{dx}{dt} = k(a - x)^{2}$$

On integrating,

$$\int \frac{dx}{(a-x)^2} = k \int dt$$

$$\therefore \frac{1}{(a-x)} = kt + c \qquad ...(i)$$

where c is the integrating constant

When
$$t = 0$$
, $x = 0$, $\therefore c = \frac{1}{a}$

Substituting the value of c in Eq. (i),

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

or
$$kt = \frac{1}{(a-x)} - \frac{1}{a}$$

or
$$t = \frac{1}{k} \cdot \frac{x}{a(a-x)}$$
...(ii)

Case II: When the two reactants have different concentrations

$$A + B \longrightarrow Products$$
At $t = 0$ a b 0
At $t = t$ $(a - x)$ $(b - x)$ x

$$\therefore \frac{dx}{dt} = k (a - x) (b - x)$$

This equation on integration gives:

$$t = \frac{1}{k} \cdot \frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$$
 ...(iii)

Characteristics of Second Order Reactions

a. The value of k (velocity constant) depends on the unit of concentration. The unit of k is expressed as:
 (mol L⁻¹)⁻¹ t⁻¹ or L mol⁻¹ t⁻¹

b. Half-life period
$$(t_{1/2}) = \frac{1}{k} \cdot \frac{0.5a}{a \times 0.5a} = \frac{1}{ka}$$

Thus, half life is inversely proportional to initial concentration.

c. Second order reaction follows to the first order when one of the reactants is present in large excess.

Taking
$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$
, if $a >>> b$, then

$$(a-x) \approx a$$
 and $(a-b) \approx a$

Hence,
$$k = \frac{2.303}{ta} \log \frac{ba}{a(b-x)}$$

or
$$ka = k' = \frac{2.303}{t} \log \frac{b}{(b-x)}$$

(Since a being very large, may be treated as constant after the change)

Thus, the reaction follows first order kinetics with respect to the reactant taken relatively in small amount.

d. Some examples of second order reactions are as follows:

i. Hydrolysis of ester by an alkali (saponification): CH₃COOC₂H₅ + NaOH → CH₃COONa + C₂H₅OH

ii. The decomposition of NO_2 into NO and O_2 : $2NO_2 \longrightarrow 2NO + O_2$.

iii. Conversion of ozone into oxygen at 100° C: $2O_3 \longrightarrow 3O_2$

iv. Thermal decomposition of chlorine monoxide: $2Cl_2O \longrightarrow 2Cl_2 + O_2$ v. Reaction between persulphate (or peroxo disulphate) with I[©] ion:

with
$$I^{\odot}$$
 ion.
 $S_2O_8^{2-} + 2I^{\odot} \longrightarrow 2SO_4^{2-} + I_2$

4.7.4 THIRD ORDER REACTIONS Areaction is said to be of third order if its rate is determined by Alcae Alcae

When the concentration of all the three reactants is same of three molecules of the same reactant are involved, the rate expression is given as

$$3A \longrightarrow Products$$

$$A+B+C \longrightarrow Products$$

$$\frac{dx}{dt} = k(a - x)^3$$

On integration and solving this equation,

$$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

Characteristics of Third Order Reactions

a. Half life period:

$$t_{1/2} = \frac{1}{k} \cdot \frac{0.5a(2a - 0.5a)}{2a^2(0.5a)^2} = \frac{1}{k} \cdot \frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a} = \frac{3}{2a^2k}$$

Thus, the half life is inversely proportional to the square of initial concentration.

- b. The change in the unit of concentration changes the numerical value of k.
- c. The unit of k is expressed as (mol L^{-1})⁻² t^{-1} or L^2 mol⁻² t^{-1} .
- d. Some examples of third order reactions are as follows:
 - i. Reaction between nitric oxide and oxygen:
 - $2NO + O_2 \longrightarrow 2NO_2$
 - ii. Reaction between nitric oxide and chlorine:

$$2NO + Cl_2 \longrightarrow 2NOCl$$

- iii. Reduction of FeCl₃ by SnCl₂:
- $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow \text{SnCl}_4 + 2\text{FeCl}_2$ iv. Reaction between nitric oxide and bromine:
- $2NO + Br_2 \longrightarrow 2NaOBr$

Table 4.3 Expressions for rate constant for reactions of different orders

Reaction	Order	Rate law equation	Expression for rate constant
$A \rightarrow Products$	0	Rate = k	$k = \frac{1}{t} \left([\mathbf{A}]_0 - [\mathbf{A}] \right)$
$A \rightarrow Products$	1	Rate = $k[A]$	$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$
2A → Products	2	Rate = $k[A]^2$	$k = \frac{1}{t} \left(\frac{1}{[A]} - \frac{1}{[A]_0} \right)$

A+B → Products	2	Rate = <i>k</i> [A] [B]	$k = \frac{2.303}{t [A]_0 - [B]_0}$
			$\log \frac{[B]_0 [A]}{[A]_0 [B]}$
3A → Products	3	Rate = $k[A]^3$	$k = \frac{1}{2t} \left(\frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right)$

where $[A]_0$ and $[B]_0$ = initial concentrations of A and B, i.e., a and b.

- [A] = Concentration of A left after time t, i.e., a x, where x is the concentration decomposed.
- [B] = Concentration of B left after time t, i.e., b-x, where x is the concentration decomposed.

Table 4.4 Order of reaction and $t_{1/2}$ values along with the units of rate constant

Order	Units of k	t _{1/2} values	
Zero	mol L ⁻¹ t ⁻¹	$t_{1/2} \propto a$,	$t_{1/2} = \frac{a}{2k}$
1	t-1	$t_{1/2} \propto (a)^0$	$t_{1/2} = \frac{0.693}{k}$
2	L mol ⁻¹ t ⁻¹	$t_{1/2} \propto (a)^{-1}$	$t_{1/2} = \frac{1}{ka}$
3	L ² mol ⁻² t ⁻¹	$t_{1/2} \propto (a)^{-2}$	$t_{1/2} = \frac{3}{2ka^2}$
n	$L^{(n-1)} \operatorname{mol}^{(1-n)} t^{-1}$	$t_{1/2} \propto (a)^{1-n}$	

4.7.5 FRACTIONAL ORDER REACTIONS

In many reactions, the order of reaction w.r.t. one of the reactant is found to be non integral, e.g.

a. The reaction between H₂ and D₂:

Rate =
$$kP_{\rm H_2}(P_{\rm D_2})^{1/2}$$

b. The conversion of parahydrogen to orthohydrogen at high temperature: rate = $k(P_{H_2})^{1.5}$

The non-integer values are generally due to the complex nature of reactions which involves more than one elementary step. The overall rate law is obtained by combining the rates of individual elementary steps.

4.7.6 NEGATIVE ORDER REACTIONS

Sometimes, the rate of a reaction decreases as the concentration of one of the constituent is increased, e.g., transformation of ozone into oxygen, i.e.,

$$2O_3 \longrightarrow 3O_2$$

$$-\frac{1}{2}\frac{d[O_3]}{dt} = k\frac{[O_3]^2}{[O_2]} = k[O_3]^2[O_2]^{-1}$$

Thus, order with respect to oxygen is -1.

It should be made clear that negative orders such as zero order and fractional orders are obtained whenever the desired reaction does not occur in single elementary step.

ILLUSTRATION 4.61

For a first order reaction, calculate the ratio between the time taken to complete 3/4th of the reaction and time taken to complete half of the reaction.

Sol.
$$t_{1/2} = \frac{0.69}{k}$$
, $t_{314} = t_{75\%}$
 $t_{3/4} = \frac{2.303}{k} \log \frac{a}{\left(a - \frac{3a}{4}\right)}$
 $= \frac{2.303}{k} \log 4$
 $= \frac{2.303}{k} \times 2 \times 0.3010 = \frac{0.69 \times 2}{k}$
 $\frac{t_{3/4}}{t_{1/2}} = \frac{0.69 \times 2}{k} \times \frac{k}{0.69} \Rightarrow t_{3/4} = 2t_{1/2}$

Alternate Method

Use direct relation.

$$\frac{t_{75\%}}{t_{1/2}} = \frac{\log\left(\frac{100}{100 - 75}\right)}{0.3} = \frac{2\log 2}{0.3} = \frac{2 \times 0.3}{0.3} = 2$$

$$\therefore t_{75\%} = 2t_{1/2}$$

ILLUSTRATION 4.62

For the following reaction:

$$2A + B + C \longrightarrow A_2B + C$$

The rate law has been determined to be

Rate =
$$k[A][B]^2$$
 with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} L^2 \text{ s}^{-1}$

For this reaction, determine the initial rate of the reaction with $[A] = 0.1 \text{ mol } L^{-1}$, $[B] = 0.2 \text{ mol } L^{-1}$, $C = 0.8 \text{ mol } L^{-1}$.

Determine the rate after 0.04 mol L⁻¹ of A has reacted.

Sol.

a.
$$2A + B + C \longrightarrow A_2B + C$$

Rate = $k [A] [B]^2$
 $r = 2.0 \times 10^{-6} \times [0.1] \times [0.2]^2$
= $8 \times 10^{-9} \text{ mol} \cdot L^{-1} \text{ s}^{-1}$
b. $\frac{-d[A]}{2dt} = \frac{-d[B]}{dt} = \frac{-d[C]}{dt} = \frac{d[A_2B]}{dt} = \frac{d[C]}{dt}$
 $[A]_{\text{initial}} = 0.1 \text{ M}; \quad [A]_{\text{reacted}} = 0.04 \text{ M}$
 $[A]_{\text{left}} = 0.1 - 0.04 = 0.06 \text{ mol } L^{-1}$
 $\frac{-d[A]}{2dt} = \frac{-d[B]}{dt}$
 $\therefore \frac{-d[B]}{dt} = \frac{1}{2} \times \frac{-d[A]}{dt} = \frac{1}{2} \times 0.04 = 0.02 \text{ M s}^{-1}$

[B]_{initial} = 0.2 M
[B]_{left} = 0.2 - 0.02 = 0.18 mol L⁻¹

$$\therefore r = k[A] [B]^2 = 2.0 \times 10^{-6} (0.06) (0.18)^2$$
= 3.88 × 10⁻⁹ mol · L⁻¹ s⁻¹

ILLUSTRATION 4.63

A drug becomes ineffective after 30% decomposition. The original concentration of a sample was 5 mg mL⁻¹ which becomes 4.2 mg mL⁻¹ during 20 months. Assuming the decomposition of first order, calculate the expiry time of the drug in month. What is the half life of the product?

Sol.
$$k = \frac{2.303}{t} \log \left(\frac{a}{a - x} \right) = \frac{2.303}{20} \log \left(\frac{5}{4.2} \right)$$

= 0.00872 month⁻¹

Expiry time t may be calculated as:

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$0.00872 = \frac{2.303}{t} \log \frac{100}{70} \Rightarrow t = 40.9 \approx 41 \text{ months}$$

$$t_{1/2} = \frac{0.693}{0.00872} = 79.4 \text{ months}$$

ILLUSTRATION 4.64

The half life of a first order reaction is 60 min. How long will it take to consume 90% of the reactant?

Sol. For the first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60} = 11.55 \times 10^{-3} \text{ min}^{-1}$$

Applying first order kinetic equation,

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)}$$
Given: $a = 100, x = 90$, i.e., $(a-x) = (100-90) = 10$
Hence, $t = \frac{2.303}{11.5 \times 10^{-3}} \log 10 = 200 \text{ min}$

Alternate method

$$t_{1/2} = 60 \text{ min}$$

$$\frac{t_{90\%}}{t_{1/2}} = \frac{\log\left(\frac{100}{100 - 90}\right)}{0.3}$$

$$t_{90\%} = \frac{t_{1/2} \times \log 10}{0.3} = \frac{60 \times 1}{0.3} = 200 \text{ min}$$

ILLUSTRATION 4.65

A first order reaction has a rate constant of 15×10^{-3} s⁻¹. How long will 5.0 g of this reaction take to reduce to 3.0 g?

Sol. Applying first order kinetic equation,

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)}$$

$$k = 5 \times 10^{-3} \text{ s}^{-1}, a = 5 \text{ g}, (a - x) = 3 \text{ g}$$

$$t = \frac{2.303}{5 \times 10^{-3}} \log \frac{5}{3} = 34.07 \text{ s}$$

ILLUSTRATION 4.66

If in a reaction A \rightarrow Products, the concentrations of reactant A are c_0 , ac_0 , a^2c_0 , a^3c_0 , ... after time interval 0, t, 2t, 3t ... where a is constant, given, 0 < a < 1, show that the reaction is of first order. Also calculate the relation in k, a, and t.

Sol. $k = \frac{2.303}{t} \log \frac{a}{a - x}$

If
$$t = t$$
, $a = c_0$ and $(a - x) = ac_0$

$$k = \frac{2.303}{t} \log \frac{c_0}{ac_0} = \frac{2.303}{t} \log \frac{1}{a}$$

If
$$t = 2t$$
, $a = c_0$, $(a - x) = a^2 c_0$

$$k = \frac{2.303}{2t} \log \frac{c_0}{a^2 c_0} = \frac{2.303}{t} \log \frac{1}{a}$$

If
$$t = 3t$$
, $k = \frac{2.303}{3t} \log \frac{c_0}{a^3 c_0} = \frac{2.303}{t} \log \frac{1}{a}$

k comes constant and thus it is a first order reaction.

Also
$$k = \frac{2.303}{t} \log \frac{1}{a}$$

ILLUSTRATION 4.67

Reaction A follows first order kinetics and reaction B follows second order kinetics. If their half lives are equal, compare their rates (i) at the start of the reaction and (ii) after lapse of one half life.

Sol. For the first order reaction A, half life
$$t_{50}(1) = \frac{0.693}{k_1}$$

and for the second order reaction B, half life $t_{50}(2) = \frac{1}{k_2 a}$

But
$$t_{50}(1) = t_{50}(2)$$
 (given)

$$\therefore \frac{0.693}{k_1} = \frac{1}{k_2 a}$$

$$\frac{k_1}{k_2 a} = 0.693$$
 ...(i)

i. Rate at the start of reaction A, $r_1 = k_1 a$...first order and rate at the start of reaction B, $r_2 = k_2 a^2$...second order

Hence
$$\frac{r_1}{r_2} = \frac{k_1 a}{k_2 a^2} = \frac{k_1}{k_2 a} = 0.693$$
 by Eq. (i)

ii. Rate after one half life when the concentration of the reactant is reduced to (a/2)

For reaction A,
$$r'_1 = k_1 \left(\frac{a}{2}\right)$$

and for reaction B,
$$r'_2 = k_2 \left(\frac{a}{2}\right)^2 = \frac{k_2 a^2}{4}$$

Hence,
$$\frac{r'_1}{r'_2} = \frac{2k_1}{k_2a} = 2 \times 0.693 = 1.386$$

ILLUSTRATION 4.68

For the reaction of I, II, and III orders, $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}_3$ when concentrations are expressed in mole L⁻¹. What will be the relation in \mathbf{k}_1 , \mathbf{k}_2 , \mathbf{k}_3 , if the concentrations are expressed in mol mL⁻¹?

Sol.
$$k \propto [a]^{1-n}$$

For first order: $k \propto [a]^{1-1} \Rightarrow k \propto 1$

So k is constant and is independent of units of "a."

$$\therefore k_1 = k'_1 \qquad \dots (i)$$

For second order: $k \propto [a]^{1-2} \propto [a]^{-1}$

 $k_2 \propto [a]^{-1}$ when units of a in mol L⁻¹.

 $k_2 \propto [a]^{-1}$ when units of a in mol mL⁻¹.

⇒ $k'_2 \propto [a \times 10^3]^{-1}$ when a in mol mL⁻¹. $\propto [a]^{-1} [10^3]^{-1}$

$$k'_{2} \propto k_{2} \times 10^{-3}$$

$$\therefore k_2 \propto \frac{k'_2}{10^{-3}} \propto k'_2 \times 10^3$$

$$\therefore k_2 \propto k'_2 \times 10^3 \qquad \dots (ii)$$

For third order: $k \propto [a]^{1-3} \propto [a]^{-2}$

 $k_3 \propto [a]^{-2}$ when a is in mol L⁻¹

 $k'_3 \propto [a]^{-2}$ when a is in mol mL⁻¹

$$\Rightarrow k'_3 \propto [a \times 10^3]^{-2}$$

$$k'_3 \propto [a]^{-2} [10^{-6}]$$

$$\Rightarrow k'_3 \propto [k_3 \times 10^{-6}]$$

$$\therefore k_3 \propto \frac{k'_3}{10^{-6}}$$

$$k_3 \propto {k'}_3 \times 10^6 \qquad \qquad ...(iii)$$

Since
$$k_1 = k_2 = k_3$$

$$k'_1 = k'_2 \times 10^3 = k'_3 \times 10^6$$

ILLUSTRATION 4.69

Starting with one mole of a compound A, it is found that the reaction is 3/4 completed in 1 hr. Calculate the rate constant if the reaction is of

- a. First order
- b. Second order

Sol.
$$a = 1$$
 mole, $x = 3/4$ mole, $t = 1$ hr

a. First order: $k = \frac{2.303}{1} \log \frac{1}{1 - \frac{3}{4}}$

$$= \frac{2.303}{1} \log 4 = 1.386 \, hr^{-1}$$

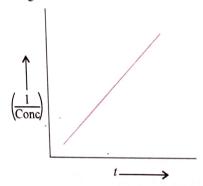
b. Second order:
$$k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

= $\frac{1}{t} \times \frac{3/4}{1 \times (1-3/4)} = 3$

$$k = 3 \text{ L mol}^{-1} \text{ hr}^{-1}$$

ILLUSTRATION 4.70

In the decomposition of N2O5, the plot between the reciprocal of concentration of the reactant and the time was found to be linear as shown in the figure below. Determine the order of reaction.



Sol. Reaction is of second order

$$k = \frac{1}{t} \frac{x}{(a-x)}$$

$$t = \frac{1}{k} \frac{x}{(a-x)}$$

$$t = \frac{1}{k} \frac{x}{(a-x)}$$

$$t \text{ vs}\left(\frac{1}{\text{Conc}}\right)$$
 graph is linear.

ILLUSTRATION 4.71

For a reaction at 800°C

 $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$, the following data were obtained:

		70000	e stanica.
	[NO] × 10 ⁻⁴	$[\text{H}_2] \times 10^{-3}$	$-\frac{1}{2}\frac{d [\text{NO}]}{dt} \times 10^{-4}$
	(M)	(M)	(mol L ⁻¹ min ⁻¹)
i.	1.5	4.0	4.4
ii.	1.5	2.0	2.2
iii.	0.5	2.0	0.244

What is the order of this reaction with respect to NO and H₂? Also calculate the rate constant.

Sol.
$$r = k [NO]^{\alpha} [H_2]^{\beta}$$

[NO]
$$\times$$
 10⁻⁴ = 1.5

$$\therefore [NO] = 1.5 \times 10^4$$

$$[H_2] \times 10^{-3} = 4.0$$

$$\therefore [H_2] = 4.0 \times 10^3$$

$$-\frac{1}{2}\frac{d[NO]}{dt} \times 10^{-4} = 4.4$$

$$\therefore -\frac{1}{2} \frac{d [\text{NO}]}{dt} = 4.4 \times 10^4$$

From data (i), (ii), and (iii),

$$4.4 \times 10^4 = k \left[1.5 \times 10^4\right]^{\alpha} \left[4.0 \times 10^3\right]^{\beta}$$

$$2.2 \times 10^4 = k \left[1.5 \times 10^4\right]^{\alpha} \left[2.0 \times 10^3\right]^{\beta}$$

$$0.24 \times 10^4 = k [0.5 \times 10^4]^{\alpha} [2.0 \times 10^3]^{\beta}$$

Solving
$$\alpha = 2$$
, $\beta = 1$

$$4.4 \times 10^4 = k \left[1.5 \times 10^4\right]^2 \left[4.0 \times 10^3\right]^1$$

$$k = 4.88 \times 10^{-8} \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

ILLUSTRATION 4.72

A drop of solution (volume 0.05 mL) contains 3×10^{-6} male H^{\oplus} ions. If the rate constant \times 10⁷ mol L⁻¹ s⁻¹, how long would it take for H^{\oplus} ions in the drop of disappear?

Sol. Concentration of drop =
$$\frac{\text{Mole}}{\text{Volume in mL}} \times 1000$$

$$= \frac{3 \times 10^{-6}}{0.05} \times 1000 = 0.06 \, \text{mol} \, \text{L}^{-1}$$

Rate of disappearance =
$$\frac{\text{Conc change}}{\text{Time}}$$

$$1 \times 10^7 = \frac{0.06}{\text{Time}}$$

Time =
$$6 \times 10^9$$
 s

Second method

Units of $k \pmod{L^{-1} s^{-1}}$ suggest it is a zero order reaction.

$$\therefore \text{ For zero order} = t = \frac{x}{k} = \frac{\text{Conc used}}{\text{Rate constant}}$$

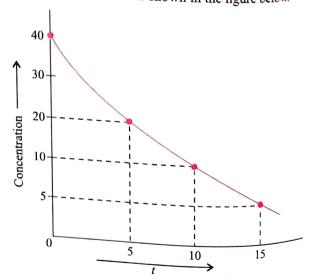
$$0.05 \text{ mL has} = 3 \times 10^{-6} \text{ mol of H}^{\oplus}$$

1000 mL has =
$$\frac{3 \times 10^{-6}}{0.05} \times 10^3 = 0.6 \times 10^{-1} \text{ mol L}^{-1}$$

$$t = \frac{0.6 \times 10^{-1}}{1.0 \times 10^{7}} = 6 \times 10^{-9} \text{ s}$$

ILLUSTRATION 4.73

For a reaction, a graph was plotted between reactant concentration c and time as shown in the figure below.



Identify the order of the reaction with respect to the reactant Can the concentration of the reactant be theoretically zero after infinite time?

From graph, it is evident that Concentration of 40 reduces to 20 in 5 min.

b. 20 reduces to 10 in 5 min.

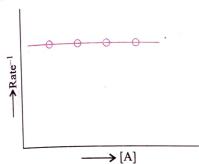
c. 10 reduces to 5 in 5 min. half life is independent of concentration which is i.e., man which is characteristic of first order. In first order, the concentration of the reactant can never be the theoretically zero.

ILLUSTRATION 4.74

 $2A+3B \longrightarrow Product$

8. What is the molecularity of the reaction?

b. What is order w.r.t. A and B in the following cases:



i. When
$$\left(\frac{dx}{dt}\right) = k$$
 [A] and B is in excess.

ii. When
$$\left(\frac{dx}{dt}\right) = k [B]^2$$
 and graph is true.

iii. When the rate is doubled, then the concentration of A is doubled, and the rate is eight times when the concentration of A and B is doubled.

a. In reaction $2A + 3B \longrightarrow Product$ Molecularity = 5 (5 molecules are colliding 2A and 3B)

b. i. When $\frac{dx}{dt} = k$ [A], order w.r.t. A = 1 and order w.r.t

ii. When
$$\left(\frac{dx}{dt}\right) = k \, [B]^2$$

Order w.r.t. A = 0, w.r.t. B = 2

iii. Rate
$$(r_1) = k[A]^{\alpha} [B]^{\beta}$$

Case (i)
$$2r_1 = k[2A]^{\alpha} [B]^{\beta}$$
 ...(i)

Case (ii)
$$8r_1 = k[2A]^{\alpha} [2B]^{\beta}$$
 ...(ii)

From Eqs. (i) and (ii), we get

 $\alpha = 1, \beta = 2$

 \therefore Order w.r.t. A = 1

Order w.r.t. B = 2

4.8 EXPERIMENTAL DETERMINATION OF ORDER OF REACTION

There are several methods available for determining the order of a reaction. All these methods are based on the use of differential or integral rate equations given in Section 4.7.

4.8.1 INITIAL RATE METHOD

In this method, the initial rate of a reaction is determined by varying the concentration of one of the reactants while others are kept constant. The initial rate r_0 is determined either numerically or from the slope of the curve vs time at t = 0. Thus, the initial rate of the reaction is given by

$$r_0 = \text{rate} = k [A]_0^a [B]_0^b [C]_0^c$$
 ...(i)

If [B] and [C] are kept constant, then

$$r_0 = k_0 [A]_0^a$$
, where $k_0 = k [B]_0^b [C]_0^c$...(ii)

The value of a can be determined by inspecting the rate at different values of [A]. Alternatively, if we know the initial rates at two different concentrations of A, we have

$$(r_0)_1 = k_0 [A_0]_1^a$$
 ...(iii)

$$(r_0)_2 = k_0 [A_0]_2^a$$
 ...(iv)

where $(r_0)_1$ and $(r_0)_2$ are the initial rates of reaction when the initial concentration of \tilde{A} is $[A_0]_1$ and $[A_0]_2$, respectively. Dividing Eq. (iii) by Eq. (iv), we get

$$(r_0)_1/(r_0)_2 = \{[A_0]_1/[A_0]_2\}^a$$
 ...(v)

Taking log on both sides, we obtain

$$\log \left[(r_0)_1 / (r_0)_2 \right] = a \log \left\{ \left[A_0 \right]_1 / \left[A_0 \right]_2 \right\}$$

$$a = \frac{\log [(r_0)_1/(r_0)_2]}{\log [[A_0]_1/[A_0]_2]} \dots (vi)$$

Thus, the order of reaction with respect to A can be determined. In the same manner, the order of reaction with respect to other reactants can also be determined and the overall order of the reaction is the sum of all the exponents in Eq. (i).

i.e., order of reaction, $n = a + b + c + \cdots$

4.8.2 Use of Integrated Rate Equations

This method is also known as the method of trial and error. The kinetic data is fitted to different integrated rate equations. Wherever the data fits with the equation for the correct order of reaction, it will give the constant value of rate constant for all data points (concentration at different times). These equations also lead to straight lines when appropriate function of the concentration is plotted against time t. For example, for zero order reaction, a plot between concentration and time gives a straight line with slope of the line equal to -k. Similarly, for the first order reaction a graph between ln [R] against t gives a straight line with slope equal to

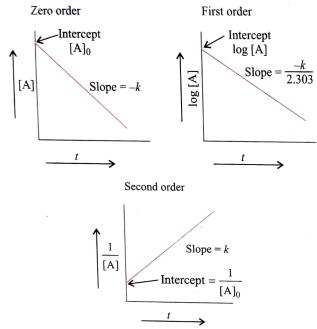
For a general reaction: $A \longrightarrow Products$, the integrated rate equation for zero, first, and second order reaction are given in Table 4.5.

Table 4.5 Integrated rate equation for different order of a reaction

Type of reaction	Equation corresponding to $y = mx + c$	Linear plot	Slope	Intercept
Zero order $(rate = k)$	$[A] = -kt + [A]_0$	[A] vs <i>t</i>	-k	[A] ₀

First order (rate = $k[A]$)	log [A] =	log [A]	$-\frac{kt}{2.303}$	log [A] ₀
,	$-\frac{k}{2.303} + \log [A]_0$	vs t		
Second order	1 [A]	$\frac{1}{[A]}$ vs t	k	$\frac{1}{[A]_0}$
$(\text{rate} \\ = k[A]^2)$	$= kt + \frac{1}{[A]_0}$			

It is clear from the above relations that the straight lines are obtained form a plot of [A] versus t for a zero order reaction, of log [A] versus t for a first order reaction, and of 1/[A] versus t for second order reaction as shown below:



These curves also help to calculate the value of k from the slope of the straight line.

ILLUSTRATION 4.75

For the hypothetical reaction

$$2A + B \longrightarrow Products$$

following data are obtained:

Experiment number	Initial conc of (A) (mol L ⁻¹)	Initial conc of (B) (mol L ⁻¹)	Initial rate mol L ⁻¹ s ⁻¹
1	0.10	0.20	3×10^2
2	0.30	0.40	3.6×10^{3}
3	0.30	0.80	1.44×10^{4}
4	0.10	0.40	
5	0.20	0.60	
6	0.30	1.20	

Find out how the rate of the reaction depends upon the concentration of A and B and fill in the blanks given in the table.

Sol. From experiments (2) and (3), it is clear that when the concentration of A is kept constant and that of B is doubled, of second order with respect to B.

Similarly, from experiments (1) and (2), it is observed that of B two times, the rate becomes 12 times. Hence, the reaction is of first order with respect to A.

Thus, the rate law for the reaction is

Rate =
$$k [A] [B]^2$$

Substituting the values of experiment (1) in the rate equalion $3 \times 10^2 = k[0.10] [0.20]^2$

or
$$k = \frac{3 \times 10^2}{[0.10][0.20]^2} = 7.5 \times 10^4 \,\mathrm{L}^2 \,\mathrm{mol}^{-2} \,\mathrm{s}^{-1}$$

Experiment (4): Rate =
$$k [0.10] [0.40]^2$$

= $7.5 \times 10^4 \times 0.10 \times 0.40 \times 0.40$

Experiment (5): Rate =
$$k [0.20] [0.60]^2$$

= $7.5 \times 10^4 \times 0.20 \times 0.60 \times 0.60$
= $5.4 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$

Experiment (6): Rate =
$$k [0.30] [1.20]^2$$

= $7.5 \times 10^4 \times 0.30 \times 1.20 \times 1.20$
= $3.24 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$

ILLUSTRATION 4.76

The data for the reaction: $A + B \xrightarrow{k} C$.

Experiment	$[A]_0$	$[B]_0$	Initial rate
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

The rate law corresponding to the above data is

a. Rate =
$$k[B]^3$$

b. Rate =
$$k[B]^4$$

c. Rate =
$$k[A][B]^3$$

d. Rate =
$$k[A]^2[B]^2$$

Sol.

a. From experiments 1 and 4 (when $[A]_0$ is same), when $[B]_0$ is doubled, rate becomes 8 times. Thus, rate $x[B]_0$. From experiments 1 and 3 (when $[B]_0$ is same), when $[A]_0$ is doubled, rate remains same. Thus, rate $x[A]_0$ is doubled, rate remains same. Thus, rate $x[A]_0$ is Rate = $x[A]_0$ $[B]_3$

ILLUSTRATION 4.77

Rate of a reaction $A + B \longrightarrow Product$, is given as a function of A and B.

[A] (mol L ⁻¹)	(B) (mol L ⁻¹)	Initial rate (mol L ⁻¹ min ⁻¹)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and with Determine Perspect to B. What is the half life of A in the reaction?

Let the rate of reaction be

Rate =
$$k [A]^x [B]^y$$

From the data given, it is clear that by doubling the concentration of A, the rate also becomes double when B is kept constant. Thus, the rate is directly proportional to concentration of A.

Rate
$$\propto$$
 [A], i.e., $x = 1$

or the order of reaction w.r.t. to A is 1.

When the concentration of A is kept constant and the concentration of B is doubled, the rate does not change, i.e., y = 0; or the order of reaction w.r.t. to B is zero.

Thus, reaction rate,
$$-\frac{dx}{dt} = k [A]$$

Again
$$k = \frac{0.005}{0.01} = 0.5 \text{ min}^{-1}$$

Half life of A =
$$\frac{0.693}{k} = \frac{0693}{0.5} = 1.386 \text{ min}$$

ILLUSTRATION 4.78

For a reaction in which A and B form C, the following data were obtained from three experiments:

Experiment	Initial conc (mol L-1)		Initial rate
number	[A]	[B]	$(\text{mol } L^{-1} s^{-1})$
1	0.03	0.03	0.3×10^{-4}
2	0.06	0.06	1.2×10^{-4}
3	0.06	0.09	2.7×10^{-4}

What is the rate equation of the equation and what is the value of rate constant?

Sol. Let the rate equation be $k [A]^x [B]^y$.

From experiment (1),
$$0.3 \times 10^{-4} = k [0.03]^x [0.03]^y$$
 ...(i)

From experiment (2),
$$1.2 \times 10^{-4} = k [0.06]^x [0.06]^y$$
 ..(ii)

$$\frac{1.2 \times 10^{-4}}{0.3 \times 10^{-4}} = \frac{[0.06]^x [0.06]^y}{[0.03]^x [0.03]^y}$$

$$4 = 2^x \times 2^y \qquad \dots(iii)$$

Similarly, from experiments (1) and (3),

$$2^{x} \times 3^{y} = 9 \qquad \dots (iv)$$

Solving Eq. (iii) and (iv), we get

$$x = 0, y = 2$$

Rate equation, rate = $k [B]^2$

Considering Eq. (i) again,

$$k = \frac{0.3 \times 10^{-4}}{[0.03]^2} = 3.33 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

ILLUSTRATION 4.79

The chemical reaction between mercuric chloride and potassium oxalate proceeds as under:

$$2\text{HgCl}_2 + \text{K}_2\text{C}_2\text{O}_4 \longrightarrow \text{KCl} + 2\text{CO}_2 + \text{Hg}_2\text{Cl}_2$$

The mass of Hg₂Cl₂ precipitated from different solutions in a given time at 100°C was as follows:

Experiment number	HgCl ₂ (mol L ⁻¹)	$K_2C_2O_4$ (mol L^{-1})	Time (min) (mole)	Hg ₂ Cl ₂ precipitated
1	0.0836	0.404	65	0.0068
2	0.0836	0.202	120	0.0031
3	0.0418	0.404	60	0.0032

From the data calculate order of the reaction.

Sol. Since mass ∞ moles ∞ M.

$$\therefore \text{ Rate} = k \left[\text{HgCl}_2 \right]^{\alpha} \left[\text{K}_2 \text{C}_2 \text{O}_4 \right]^{\beta}$$

$$\frac{0.0068}{65} = k \left[0.0836 \right]^{\alpha} \left[0.404 \right]^{\beta} \qquad \dots (i)$$

$$\frac{0.0068}{65} = k [0.0836]^{\alpha} [0.404]^{\beta} \qquad ...(i)$$

$$\frac{0.0031}{120} = k [0.0836]^{\alpha} [0.202]^{\beta} \qquad ...(ii)$$

$$\frac{0.0032}{60} = k [0.0418]^{\alpha} [0.404]^{\beta} \qquad \dots (iii)$$

Dividing Eq. (i) by (ii), we get $4 = 2^{\beta} \Rightarrow \beta = 2$

Dividing Eq. (i) by (iii), we get $2 = 2^{\alpha} \Rightarrow \alpha = 1$

Thus, overall order $\alpha + \beta = 3$

ILLUSTRATION 4.80

A certain radio isotope $_{\mathbf{Z}}X^{A}$ (half life = 10 days) decays to give $Z^{-2}Y^{A-4}$. If 1.0 g atom of X is kept in a sealed vessel, find the volume of helium accumulated at STP in 20 days?

Sol. Since 1.0 g atom of X = 1 mol of X =
$$a_0$$

$$ZX^A \longrightarrow Z^2Z^{A-4} + {}_2He^4$$
Initial

$$Z^{XA} \longrightarrow Z^{-2}X^{A} + 2^{\mathbf{RC}}$$
Initial 1 0 0

$$n = \text{Number of half lives} = \frac{20}{10} = 2$$

Moles of X left =
$$\left(\frac{1}{2}\right)^n \times a_0$$

$$=\left(\frac{1}{2}\right)^2 \times 1 = \frac{1}{4} \mod \Rightarrow (1-x) \mod$$

Moles of helium formed =
$$1 - \frac{1}{4} = \frac{3}{4} \mod \Rightarrow x \mod$$

$$=\frac{3}{4}\times22.4L=16.8L$$
 at STP

ILLUSTRATION 4.81

The population of India in 1988 was 800 million. What will be the population in 2000 and 2100 if there is no change in the present growth rate which is 25 per 1000 per year?

Note: Here compared to the population in the year 2000 or 2100, the population in 1988 will be less. So, consider present population (P_0) for the years 2000 and 2100 and consider population in 1988 as P_t . The population will be obtained as $P_0 > P_t$.

Sol. The equation for first order can be modified as:

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

Present population, P_0

Growth rate =
$$\frac{2.303}{\text{Time }(t)} \log \frac{\text{(for 2000)}}{\text{Population }(P_t) \text{ at time } t}$$
(for 1988)

a.
$$\frac{25}{1000} = \frac{2.303}{(2000 - 1988)} \log \frac{P_0}{P_t}$$
$$\log \frac{P_0}{P} = \frac{25 \times 12}{1000 \times 2.303} = 0.1303$$

$$\frac{P_0}{P_t}$$
 = Antilog (0.1303) = 1.350

 $P_0 = 1.350 \times P_t = 1.350 \times 800$ million = 1080 million Population in 2000 years = 1080 million

b.
$$\frac{25}{1000} = \frac{2.303}{(2100 - 1988)} = \log \frac{P_0 \text{ (for 2100)}}{P_t \text{ (for 1988)}}$$

$$\log \frac{P_0}{P_t} = \frac{25 \times 112}{1000 \times 2.303} = 1.2158$$

$$\frac{P_0}{P_t} = 1.644$$

 $P_0 = 1.644 P_t = 1.644 \times 800 \text{ million} = 1315.2 \text{ million}$ \therefore Population in 2100 = 1315.2 million

ILLUSTRATION 4.82

The experimental data for the reaction

$$2A + B_2 \longrightarrow 2AB$$
 is

Experiment	[A]	$[B_2]$	Initial rate
	M	M	$(\text{mol } L^{-1} s^{-1})$
I	0.50	0.5	1.6×10^{-4}
II	0.50	1.0	3.2×10^{-4}
III	1.00	1.0	3.2 × 10 ⁻⁴

Write the most probable rate equation for the reaction giving reason for you answer.

Sol. First method

$$2A + B_2 \longrightarrow 2AB$$

In experiments I and II, the concentration of A is constant, but the concentration of [B₂] is doubled and the rate is also doubled

$$\therefore r \propto [B_2]^1$$

Similarly, in experiments II and III, the concentration of $[B_2]$ is constant, but the concentration of [A] is doubled, but the rate of does not change.

$$r \propto [A]^0$$

:. Rate law is

$$r \propto [B_2] [A]^0$$

or
$$r = k [B_2]$$

Second method

Let the rate of reaction is

$$r = k [A]^{\alpha} [B_2]^{\beta}$$

$$\therefore r_1 = 1.6 \times 10^{-4} = k [0.5]^{\alpha} [0.5]^{\beta}$$
 ...(i)

$$r_2 = 3.2 \times 10^{-4} = k [0.5]^{\alpha} [1.0]^{\beta}$$
 ...(ii)

$$r_3 = 3.2 \times 10^{-4} = k [1.0]^{\alpha} [1.0]^{\beta}$$
 ...(iii)

Divide equation (ii) by (i),

$$\frac{3.2 \times 10^{-4}}{1.6 \times 10^{-4}} = \frac{k \left[0.5\right]^{\alpha} \left[1.0\right]^{\beta}}{k \left[0.5\right]^{\alpha} \left[0.5\right]^{\beta}}$$

$$(2)^1 = (2)^\beta \Rightarrow \beta = 1$$

Similarly, divide Eq. (iii) by (ii),

$$\frac{3.2 \times 10^{-4}}{3.2 \times 10^{-4}} = \frac{k [1.0]^{\alpha} [1.0]^{\beta}}{k [0.5]^{\alpha} [1.0]^{\beta}}$$

$$1 = (2)^{\alpha} \Rightarrow (2)^{0} = (2)^{\alpha} \Rightarrow \alpha = 0$$

:. Rate =
$$k [A]^0 [B_2]^1 = k [B_2]$$

ILLUSTRATION 4.83

From the gaseous reaction

 $2A + B_2 \longrightarrow 2AB$, the following rate data were obtained at 300 K.

	Rate of disappearance of	Concentration	
	B ₂ (mol L ⁻¹ min ⁻¹)	[A] M	[B ₂] M
i	1.8×10^{-3}	0.015	0.15
ii	1.08×10^{-2}	0.090	0.15
iii	5.4×10^{-3}	0.015	0.45

Calculate the rate constant for the reaction and the rate of formation of AB when [A] is 0.02 and [B₂] is 0.04 mol L⁻¹ at 300 K.

Sol.
$$2A + B_2 \longrightarrow 2AB$$

Let the rate of reaction is

$$r = k [A]^{\alpha} [B_2]^{\beta}$$

$$r_1 = 1.8 \times 10^{-3} = k[0.015]^{\alpha} \cdot [0.15]^{\beta}$$

...(i)

$$r_2 = 1.08 \times 10^{-2} = k[0.09]^{\alpha} \cdot [0.15]^{\beta}$$

$$r_3 = 5.4 \times 10^{-3} = k[0.015]^{\alpha} [0.45]^{\beta}$$

$$\frac{1.08 \times 10^{-2}}{1.8 \times 10^{-3}} = \frac{k[0.09]^{\alpha} [0.15]^{\beta}}{k[0.015]^{\alpha} [0.15]^{\beta}} \Rightarrow (6)^{1} = (6)^{\alpha} \Rightarrow \alpha^{=1}$$

Substitute the value of r, [A], and [B $_2$] in Eq. (i) and calculate

$$\frac{k}{1.8 \times 10^{-3}} = k[0.015]^{1} [0.15]^{1}$$

$$1.8 \times 10^{-1}$$
 min⁻¹ (unit of second order reaction)

$$_{2A} + B_2 \longrightarrow 2AB$$

$$\frac{-d[A]}{2dt} = \frac{-d[B_2]}{dt} = \frac{+d[AB]}{2dt}$$

$$\underbrace{\frac{d[AB]}{dt}} = 2 \times \frac{-[B_2]}{dt}$$

Rate =
$$\frac{-[B_2]}{dt}$$
 = $k[A]^1 [B_2]^1 = 0.8 \times (0.02)^1 (0.04)$
= $0.64 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

$$\frac{d[AB]}{dt} = 2 \times 0.64 \times 10^{-3}$$
$$= 1.28 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

ILLUSTRATION 4.84

For a chemical reaction $A \longrightarrow B$, it is found that the rate of reaciton doubles when the concentration of A is increased 4 times. What is the order of reaction? Suggest the rate law also.

$$\mathbf{Sol.} \quad r_1 = k[\mathbf{A}]^n \qquad \dots (\mathbf{i})$$

$$r_2 = 2r_1 = k[4A]^n$$
 ...(ii)

Divide Eq. (ii) by Eq. (i)

$$\frac{2r_1}{r_1} = \frac{k[4A]^n}{k[A]^n}$$

$$2 = (4)^n \implies (2)^1 = (2)^{2n} \implies 2n = 1 \implies n = \frac{1}{2}$$

Order of reaction =
$$\frac{1}{2}$$
 \Rightarrow Rate = $k[A]^{\frac{1}{2}}$

LLUSTRATION 4.85

For a hypothetical reaction $A + B \longrightarrow C$, suggest the rate law and order from the following data:

Experiment	[A] (mol L ⁻¹)	[B] (mol L ⁻¹)	Rate of reaction (mol L ⁻¹ s ⁻¹) 3.0×10^{-3}
I	0.25	0.25	
II	0.50	0.25	6.0×10^{-3}
III	0.50	0.50	1.20×10^{-2}

Let the rate of the reaction is

$$r = k \left[\mathbf{A} \right]^{y} \left[\mathbf{B} \right]^{y} \qquad \dots (i)$$

$$r_1 = 3.0 \times 10^{-3} = k [0.25]^x [0.25]^y$$
 ...(ii)

$$r_2 = 6.0 \times 10^{-3} = k [0.5]^x [0.25]^y$$

$$r_3 = 1.20 \times 10^{-2} = k [0.5]^x [0.5]^y$$
 ...(iii)

Divide equation (ii) by (i)

$$\frac{6.0 \times 10^{-3}}{3.0 \times 10^{-3}} = \frac{k [0.5]^{x} [0.25]^{y}}{k [0.25]^{x} [0.25]^{y}}$$

$$(2)^1 = (2)^x \Rightarrow x = 1$$

Divide Eq. (iii) by Eq. (ii)

$$\frac{1.20 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k [0.5]^{x} [0.5]^{y}}{k [0.5]^{x} [0.25]^{y}}$$

$$\therefore (2)^1 = (2)^y \Rightarrow y = 1$$

$$\therefore r = k [A]^1 [B]^1$$

Total order = 1 + 1 = 2

ILLUSTRATION 4.86

For the chemical reaction

$$A + B + C \longrightarrow E$$
,

the rate of reaction is doubled when the concentration of B was doubled, and when the concentration of both A and B were doubled the rate becomes doubled and when the concentration of both B and C were doubled the rate becomes quadrupled. What is order with respect A, B, and C and total order?

Sol.
$$r_1 = k[A]^x [B]^y [C]^z$$
 ...(i)

$$r_2 = 2r_1 = k[A]^x [2B]^y [C]^z$$
 ...(ii)

$$r_3 = 2r_1 = k[2A]^x [2B]^y [C]^z$$
 ...(iii)

$$r_A = 4r_1 = k[A]^x [2B]^y [2C]^z$$
 ...(iv)

Sove for x, y, and z, x = 0, y = 1, z = 1

Order w.r.t. [A] = 0, [B] = 1, [C] = 1

Total order = 0 + 1 + 1 = 2

ILLUSTRATION 4.87

For the chemical reaction $A + 2B \longrightarrow C$, the rate of reaction is increased by 2.82 times when the concentration of A is doubled and increased by 9 times when the concentration of B was tripled. What is the order with respect to B and A and total order?

Sol. $A + 2B \longrightarrow C$

$$r_1 = k [A]^x [B]^y \qquad \dots (i)$$

$$r_2 = 2.82r_1 = k [2A]^x [B]^y$$
 ...(ii)

$$r_3 = 9r_1 = k[A]^x [3B]^y$$
 ...(iii)

Divide Eq. (ii) by Eq. (i),

$$\frac{2.82r_{\rm i}}{r_{\rm i}} = \frac{k[2A]^x [B]^y}{k[A]^x [B]^y}$$

$$2.82 = (2)^x \Rightarrow (2)^{3/2} = (2)^x \Rightarrow x = 3/2$$

Divide Eq. (iii) by Eq. (i),

$$\frac{9r_1}{r_1} = \frac{k[A]^x [3B]^y}{k[A]^x [B]^y}$$

$$9 = (3)^y \Rightarrow (3)^2 = (3)^y \Rightarrow y = 2$$

Order w.r.t
$$B = 2$$
 order w.r.t. $A = 3/2$

Total order =
$$2 + \frac{3}{2} = \frac{7}{2}$$

Note: 1. If rate increases by 2.82 times, order is 3/2.

2. If rate increases by 5.6 times, order is 5/2.

ILLUSTRATION 4.88

The rate of a gaseous reaction is given by the expression $k [A]^2 [B]^3$. The volume of the reaction vessel is suddenly reduced to one-half of the initial volume. The reaction rate relative to the original rate will be

Sol. c. Rate =
$$k[A]^2 [B]^3$$

When the volume is halved, the concentration will become double.

:. Rate =
$$k [2A]^2 [2B]^3$$

= $32k [A]^2 [B]^3$

=
$$32 \times \text{Original rate from Eq. (i)}$$
.

ILLUSTRATION 4.89

by a factor of 1.837 when the concentration of A is increased by 1.5 time. The order of reaction with respect to A is:

Sol. b. Rate =
$$k [A]^n$$

$$1.837 \times \text{Rate} = k [1.5A]^n$$

Dividing Eq. (ii) by Eq. (i),

$$1.837 = (1.5)^n$$

$$n = 3/2$$

(Solving by logarithmic method)

ILLUSTRATION 4.90

The rate of the reaction

$$3A + 2B \longrightarrow Products$$

is given by the rate expression: Rate = $k [A] [B]^2$

If A is taken in excess, the order of the reaction would be

Sol. b. When A is taken in excess, its concentration will become constant; the rate law may, therefore, be given as:

Rate =
$$k[B]^2 \Rightarrow \text{Order} = 2$$

ILLUSTRATION 4.91

For the decomposition of HI at

1000 K (2HI \longrightarrow H₂ + I₂), following data were obtained:

[HI] (M)	Rate of decomposition of HI (mol L^{-1} s ⁻¹)
0.1	2.75×10^{-8}
0.2	11×10^{-8}
0.3	24.75×10^{-8}

The order of reaction is

Sol. b. Rate =
$$k$$
 [HI] ^{n}

$$2.75 \times 10^{-8} = k$$
 [0.1] ^{n}

$$11 \times 10^{-8} = k$$
 [0.2] ^{n}
Dividing Eq. (ii) by Eq. (i),

4.8.3 GRAPHICAL METHOD

 $4=2^n \Rightarrow n=2$

In this method, data are plotted according to integrated late equations for different order reactions. The rate of reaction in plotted versus concentration R or (a-x) or R^2 and $s_{0.01}$.

·..(ii)

a. If the rate of reaction remains constant in rate Versulconcentration graph, it means that the rate is independent of the concentration of the reactant, i.e.

Rate =
$$k [R]^0$$
 or Rate = $k(a - x)^0 = k$

Therefore, the reaction is of zero order.

b. If a straight line is obtained in rate versus concentration graph, it means that the rate is directly proportional to the concentration of the reactant, i.e.,

Rate =
$$k$$
 [R] or Rate = $k(a - x)$

Therefore, the reaction is of first order.

c. If a straight line is obtained in rate versus (concentration) graph, it means that

Rate =
$$k [R]^2$$
 or Rate = $k(a-x)^2$

Therefore, the order of reaction is 2.

d. Similarly, if we get straight line in rate versus (concentration) graph, then.

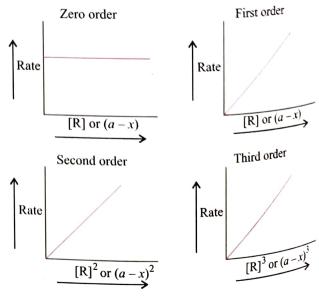
Rate =
$$k[R]^3$$
 or Rate = $k(a-x)^3$

Therefore, the order of reaction is 3.

In general, if we get a straight line by plotting the graph of rate versus (concentration)ⁿ, where n = 1, 2, 3... so on, then

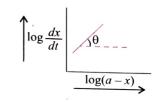
Rate = $k[R]^n$ or Rate = $k(a-x)^n$ and the order of reaction is n.

These graphs are given below:



Also if graphs are plotted in between $\log (dx/dt)$ and Also log (dx/dt), the slope of the line gives the order of reaction.

$$\int_{a}^{\log (a-x)} \frac{dx}{dt} = k(a-x)^n$$



$$y = c + mx$$

$$\log \left(\frac{dx}{dt}\right) = \log k + n \log(a - x)$$

Thus, slope =
$$n = \tan \theta$$

Table 4.6 (a) Different graphs for different order of reactions

Zero Order	First Order Second Order			
	A	Second Order	Third Order	
	$ \begin{array}{c c} \log \\ (a-x) \end{array} $	$\begin{array}{c c} \uparrow \\ \hline x \\ \hline a - x \\ \hline \end{array}$	$\frac{1}{(a-x)^2}$	
$ \uparrow \atop t_{1/2} \\ \hline $	$ \uparrow \atop t_{1/2} \\ $	$ \uparrow t_{1/2} \\ \hline $	t _{1/2}	
^	^	↑	Hyperbola	
$ \begin{array}{c c} & t_{1/2} \\ & a \\ & \end{array} $	$ \begin{array}{c c} t_{1/2} \\ \hline & \\ \hline & \\ \hline & \\ & \\ \hline & \\ & \\$	$\xrightarrow{t_{1/2}}$	$ \begin{array}{c c} & & \\$	
$\frac{dx}{dt}$ $(a-x)$	$ \begin{array}{c c} $	$\frac{dx}{dt}$ $\frac{(a-x)}{\text{Parabola}}$	$\frac{dx}{dt}$ Cubical parabola	
$\frac{dx}{dt}$	$\frac{dx}{dt}$	$\frac{dx}{dt}$ $(a-x)^2$	$\begin{array}{c c} \uparrow \\ \underline{dx} \\ dt \\ \end{array}$	
———→		(11 1)	$(a-x)^3$	

LLUSTRATION 4.92

What will be the initial rate of a reaction if its rate constant is 10^{-3} min⁻¹ and the concentration of reactant is 0.2 mol dm⁻³? How much of reactant will be converted into products in 200 min?

Sol. Since k has unit in min⁻¹, thus, the given reaction is of first order.

Now, rate = k [Concentration]¹

Rate = $10^{-3} \times [0.2]^1 = 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$

 Table 4.7(b)
 Differential equations, corresponding integral rate equation, and rate constants for various reactions

			a			$\frac{t(a-b)}{2.303}$
Nature of plot	Slope = k or $\frac{\pi}{a}$ Time Time	Slope = $k/2$, Intercept = $a/2$ Time	Slope = $-k/2.303$, Intercept = $\log a$	Slope = $k/2$, Intercept = $\frac{1}{a^{1/2}}$	Slope = k , Intercept = $\frac{1}{a}$ Time	Passing through the origin Slope=-
Na September 1	*	$\frac{1}{Z/I}(x-p)$	(x-p) gol	$\frac{1}{2\kappa(x-p)/1}$	(x-v)/[(x-q)p /(x-p)q gol
Units of k	mol dm ⁻³ s ⁻¹	mol ^{1/2} dm ^{-3/2} s ⁻¹	1-S .	$ m mol^{-3/2}dm^{3/2}s^{-1}$	$mol^{-1}dm^3s^{-1}$	$\mathrm{mol^{-1}dm^3s^{-1}}$
t _{1/2}	$\frac{a}{2k}$	$\frac{0.586}{k}a^{1/2}$	0.693 k	$\frac{0.828}{ka^{1/2}}$	$\frac{1}{ka}$	
Integral $t_{1/2}$ Units of k Nature of plot equation	$k = \frac{x}{t}$	$k = \frac{2}{t} \times [a^{1/2} - (a - x^{1/2})]$	$k = \frac{2.303}{t} \times \log \frac{a}{(a - x)}$	$k = \frac{2}{t} \times \left(\frac{1}{(a-x)^{1/2}} - \frac{1}{a^{1/2}} \right)$	$k = \frac{1}{t} \times \left(\frac{1}{(a - x)} - \frac{1}{a} \right)$	$k = \frac{2.303}{t(a-b)} \times \log \frac{b(a-x)}{a(b-x)}$
Differential	$\frac{dx}{dt} = k$	$\frac{dx}{dt} = k(a - x)^{1/2}$	$\frac{dx}{dt} = k(a - x)$	$\frac{dx}{dt} = k(a-x)^{3/2}$	$\frac{dx}{dt} = k(a - x)^2$	$\frac{dx}{dt} = k(a-x)(b-x)$
Order	0	1/2	-	3/2	. 2	2
Reaction	$A \xrightarrow{k} \text{Product}$ (a)	$\underset{(a)}{A} \xrightarrow{k} \operatorname{Product}$	$A \xrightarrow{k} \operatorname{Product}_{(a)}$	$A \xrightarrow{k} Product$ (a)	$ \begin{array}{ccc} A + B & \xrightarrow{k} \\ (a) & (a) \end{array} $ Product	$ \begin{array}{c} A + B & \stackrel{k}{\longrightarrow} \\ (a) & (b) \end{array} $ Product

Passing through Slope= $\frac{k(a+c)}{2.303}$	Slope = $2k$, Intercept = $a^{\frac{1}{2}}$ Time			Slope = $(n-1)k$, Intercept = $\frac{1}{a^{n-1}}$
mol ⁻¹ dm ³ s ⁻¹	mol ⁻² dm ⁶ s ⁻¹	$ m mol^{-2}dm^6s^{-1}$	$ m mol^{-2}dm^6s^{-1}$	$\operatorname{mol}^{-(n-1)}$ $\operatorname{dm}^{3(n-1)} \mathbf{s}^{-1}$
1	$\frac{3}{2ka^2}$		(to 10 to	$\frac{2^{(n-1)}-1}{(n-1) Ka^{(n-1)}}$
$k = \frac{2.303}{t(a+c)} \log \frac{a(c+x)}{c(a-x)}$	$k = \frac{1}{2t} \left(\frac{1}{(a-x)^2} - \frac{1}{a^2} \right)$	$k = \frac{2.303}{t(a-b)(b-c)} \times \left(\frac{a-b}{(c-a)} \right)$ $\left((b-c) \log \frac{a}{(a-x)} \right)$ $+ (c-a) \log \frac{b}{(b-x)}$ $+ (a-b) \log \frac{c}{(c-x)}$	$ \left(\frac{1}{(2b-a)}\right) \times \left\{\frac{1}{(a-2x)} - \frac{1}{a}\right\} + \frac{2-303}{(2b-a)^2} \times \log \frac{b(a-2x)}{a(b-x)} $	$\frac{1}{t(n-1)} \times \left(\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right)$
$\frac{dx}{dt} = k(a - x)(c + x)$	$\frac{dx}{dt} = k(a - x)^3$	$\frac{dx}{dt} = k(a-x)(b-x)$ $(c-x)$	$\frac{dx}{dt} = \frac{k(a - 2x)^2(b - x)}{a}$	$\frac{dx}{dt} = k(a - 2x)^2$
6	3	ĸ	т	n ≥ 2
$A + B \xrightarrow{k}$ Autocatalytic Product	$ \begin{array}{l} A + B + C \xrightarrow{k} \\ \text{(a)} \text{(a)} \text{(b)} \end{array} $ Product	$ \begin{array}{l} A + B + C \xrightarrow{k} \\ (a) (b) (c) \end{array} $ Product	$ \begin{array}{ccc} 2 & A + B & \xrightarrow{k} \\ & (a) & (b) \\ & Product \end{array} $	$A + B + C +$ (a) (a) (a) $\xrightarrow{k} $ Product

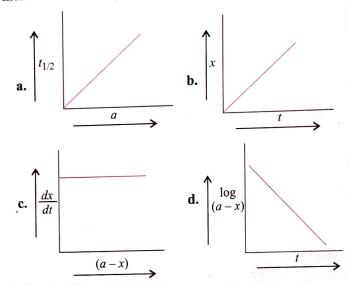
Also
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$10^{-3} = \frac{2.303}{200} \log \frac{100}{(100 - x)}$$

$$x = 18.12\%$$

ILLUSTRATION 4.93

Which of the following graphs is not for zero order reaction?



Sol.

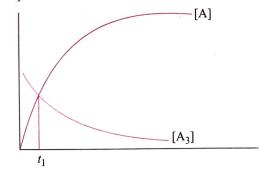
d. For a zero order reaction: dx/dt = rate of consumption of the reactant = constant. Graph a, b, and c represent zero order whereas d represents first order.

ILLUSTRATION 4.94

Using the given graph showing concentration of reactants and products as a function of time for the reaction:

$$A_3 \longrightarrow 3A$$

The time t_1 corresponds to



a. $t_{1/2}$

b. $t_{1/3}$

d. $t_{1/5}$

Sol. c.

	A ₃ –	→ 3A	When $[A]_3 = [A]$
Initial	[A] ₀	0 .	$[A]_0 - x = 3x$
Final	$[A]_0 - x$	3 <i>x</i>	or $x = \frac{[A]_0}{4} \Rightarrow t = t_{1/4}$

c. $t_{1/4}$

ILLUSTRATION 4.95

The plot of $\ln \frac{c_0}{c_0 - x}$ against t is a straight line, showing the

reaction to be a

a. Zero order reaction

b. First order reaction

c. Second order reaction

d. Half order reaction

Sol.

b. The plot of $\ln \frac{c_0}{c_0 - x}$ or $\ln \frac{[A]_0}{[A]_0 - x}$ vs t is a straight $\lim_{t \to 0} \int_0^t |a_t|^2 dt$

4.8.4 HALF LIFE METHOD OR FRACTIONAL CHANGE METHOD

A general expression for the half life $(t_{1/2})$ is given by

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where n is the order of reaction.

Starting with different initial concentrations a_1 and a_2 for the same reaction, the half lives $(t_{1/2})_1$ and $(t_{1/2})_2$, respectively, are determined. As we know,

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}}$$
 ...(i)

and
$$(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}}$$
 ...(ii)

Dividing Eq. (i) by Eq. (ii),

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \dots$$

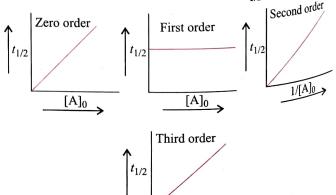
Taking logarithms on both sides,

$$\log (t_{1/2})_1 - \log (t_{1/2})_2 = (n-1) [\log a_2 - \log a_1]$$

$$(n-1) = \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log a_2 - \log a_1}$$

or
$$n = 1 + \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log a_2 - \log a_1}$$
 (iv)

Plots of half lives vs concentration $(t_{1/2} \propto a^{1-n})$



 $1/[A]_0^2$

4,8,5 OSTWALD ISOLATION METHOD

Some reactions involve a large number of reactants. In order to Some items. In order to getermine the order of such reactions a method was developed Ostwald known as isolation method. In this method, the by Usuaration of all reactants are taken in large excess except that of concentration change only for the concentration change only for this reactant is significant offer are so much in excess that practically there is no change as united to the change in their concentrations. The constant terms may be combined with the rate constant and we may write

Rate =
$$k[A]^a [B]^b [C]^c = k_0[A]^a$$

The value of a, i.e., the order of reaction with respect to A can he determined by either of the methods described above (Sections 4.8.1-4.8.5).

ILLUSTRATION 4.96

The reaction

$$CH_3COF + H_2O \longrightarrow CH_3COOH + HF$$

has been studied under the following initial conditions

١,	64	٠ I
и	N.	-

Case II

$$[H_2O]_0 = 1.00 \text{ M}$$

$$[H_2O]_0 = 0.02 \text{ M}$$

$$[CH_3COF]_0 = 0.01 \text{ M}$$

$$[CH_3COF]_0 = 0.80 \text{ M}$$

Concentrations were monitored as a function of time and are given below:

Case I		Case II		
t (min)	[CH ₃ COF] (M)	t (min)	[H ₂ O] (M)	
0	0.01000	0	0.0200	
10	0.00857	10	0.0176	
20	0.00735	20	0.0156	
40	0.00540	40	0.0122	

Determine the order of reaction and rate constant for the reaction.

Sol.

a. Let rate = $k[CH_2COF]^a [H_2O]^b$

Using Ostwald isolation method,

In first case: $[H_2O]_0 >> [CH_3COF]_0$

In second case: $[H_2O]_0 \ll [CH_3COF]_0$

In first case, determine the order of reaction w.r.t.

(CH₃COF), since $[H_2O]_0$ is very high.

The reaction is not of zero order as the rate of reaction changes with time. Using first order reaction we find:

t (min)	[CH ₃ COF] (M)	$k[H_2O]^b \text{ (min}^{-1})$ $= \frac{2.3}{t} \log \frac{[CH_3COF]}{[CH_3COF]}$	
0	0.01000	anna.	
10	0.00857	0.0154	
20	0.00735	0.0154	
40	0.00540	0.0154	

$$k[H_2O]^b = 0.0154 \text{ min}^{-1}$$

Hence, order of reaction w.r.t. $(CH_3COF) = 1$

b. Now the order of reaction w.r.t. H₂O is determined by using first order reaction.

t/min	[H ₂ O] (M)	$k[\text{CH}_3\text{COF}]^a (\text{min}^{-1})$ = $\frac{2.3}{t} \log \frac{[\text{H}_2\text{O}]_0}{[\text{H}_2\text{O}]_t}$
0	0.0200	
10	0.0176	0.0128
20	0.0156	0.0124
40	0.0122	0.0124

Average = 0.0125 min^{-1}

Hence, the reaction is first order w.r.t. (H_2O) .

$$k[CH_3COF]^1 = 0.0125 \text{ min}^{-1}$$

$$k$$
 in case II = 0.0125/0.800 M

$$= 0.0156 \text{ M}^{-1} \text{ min}^{-1}$$

k in case I

$$k [H_2O]^1 = 0.0154 \text{ min}^{-1}$$

$$k = 0.0154/1.00 \text{ M} = 0.0154 \text{ M}^{-1} \text{ min}^{-1}$$

Half Life Method

ILLUSTRATION 4.97

The half-life period and initial concentration for a reaction are as follows. What is order of reaction?

Initial concentration (M)	350	540	158
$t_{1/2}$ (hr)	425	275	941

Sol.
$$t_{1/2} \propto (a)^{1-n}$$

For I
$$\Rightarrow$$
 425 \propto (350)^{1-n} ...(i)

 $941 \propto (158)^{1-n}$.

For II
$$\Rightarrow$$
 275 \propto (540)¹⁻ⁿ

For II
$$\Rightarrow$$
 275 \propto (540)¹⁻ⁿ ...(ii)
For III \Rightarrow 941 \propto (158)¹⁻ⁿ(iii)

...(iii)

By Eqs. (i) and (ii),
$$\frac{425}{275} = \left(\frac{350}{540}\right)^{1-n}$$

Taking
$$\log \Rightarrow \log \frac{425}{275} = (1-n)\log \frac{350}{540} \Rightarrow n = 2$$

ILLUSTRATION 4.98

At a certain temperature the half change period for the catalytic decomposition of ammonia was found as follows:

Pressure (Pa)	6667	13333	26666
Half life period in hours	3.52	1.92	1.0

Calculate the order of reaction

Sol.
$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$
 (where *n* is order of reaction)

From the given data,

$$\frac{3.52}{1.92} = \left(\frac{13333}{6667}\right)^{n-1}$$
$$= (2)^{n-1}$$

 $(a \propto \text{initial pressure})$

$$\log \frac{3.52}{1.92} = (n-1) \log 2$$
$$= 0.3010 \times (n-1)$$

$$0.2632 = 0.3010 \times (n-1)$$

$$n = 1.87 \approx 2$$

Similar calculations are made between first and third observations. n comes equal to 1.908 (\approx 2).

Thus, the reaction is of second order.

ILLUSTRATION 4.99

Calculate the order of reaction from the following data:

$$2NH_3 \longrightarrow N_2 + 3H_2$$
 (reaction)

Pressure (mm Hg)	50	100	200
Half lives (min)	3.52	1.82	0.93

Sol. We know

$$n = 1 + \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log p_2 - \log p_1}$$
$$= 1 + \frac{\log 3.52 - \log 1.82}{\log 100 - \log 50}$$
$$= 1.95 \approx 2$$

Similarly, we may calculate for other set of conditions also.

ILLUSTRATION 4.100

Consider a reaction $A \longrightarrow B + C$. If the initial concentration of A was reduced from 2 M to 1 M in 1 h and from 1 M to 0.25 M in 2 h, the order of the reaction is

c. 2

d. 3

Sol

a. Half life of the given reaction is independent of initial concentration, hence it is a first order reaction.

$$\left[t_{1/2} \propto \frac{1}{a^{n-1}}\right]$$

ILLUSTRATION 4.101

For the reaction:

 $2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$, the mixture containing equimolar mixture of NO and Cl_2 gases at 0.15 atm was half changed in 175 s. In an another experiment, with an initial at 0.35 atm, the mixture was half changed in 75 s. Find the order of reaction.

Sol.
$$\left(\frac{t_2}{t_1}\right) = \left(\frac{a_1}{a_2}\right)^{n-1}$$

$$a_1 = 0.15 \text{ atm } (t_{1/2})_1 = 175 \text{ s}$$

$$a_2 = 0.35 \text{ atm } (t_{1/2})_2 = 75 \text{ s}$$

$$\frac{75}{175} = \left(\frac{0.15}{0.35}\right)^{n-1}$$

$$(0.428)^1 = (0.428)^{n-1}$$

$$\therefore n - 1 = 1$$

$$n = 2$$

ILLUSTRATION 4.102

The half-life periods of a reaction at initial concentration, 0.1 mol L^{-1} and 0.5 mol L^{-1} are 200 s and 40 s, respectively. The order of the reaction is

b. 1/2

c. 2

d, ()

Sol.

c.
$$[A]_0 = 0.1 \text{ M} \longrightarrow t_{1/2} = 200 \text{ s}$$

 $[A]_0 = 0.5 \text{ M} \longrightarrow t_{1/2} = 40 \text{ s}$

From cases (i) and (ii), we can conclude

$$t_{1/2} \propto [\mathbf{A}]_0^{-1}$$

Therefore, it is a second order reaction. **Alternatively,**

$$\left(\frac{t_2}{t_1}\right) = \left(\frac{a_1}{a_2}\right)^{n-1} \implies \left(\frac{40}{200}\right) = \left(\frac{0.1}{0.5}\right)^{n-1}$$
$$\implies \left(\frac{1}{5}\right)^1 = \left(\frac{1}{5}\right)^{n-1}$$

$$n-1=1$$

$$n=2$$

ILLUSTRATION 4.103

The half-life period of a substance is 50 min at a certain initial concentration. When the concentration is reduced to one-half of its initial concentration, the half-life period is found to be 25 min. Calculate the order of reaction.

Sol. Suppose the initial concentration in the first case $a \mod L^{-1}$. Then $[A_0]_1 = a$, $(t_{1,2})_1 = 50 \min$

$$[A_0]_2 = \frac{a}{2}, \quad (t_{1/2})_2 = 25 \text{ min}$$

We know that for a reaction of nth order

$$t_{1/2} \propto \frac{1}{\left[\mathbf{A}_0\right]^{n-1}}$$

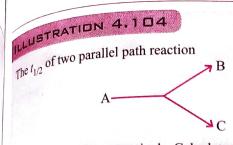
$$\therefore \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[A_0]_2^{n-1}}{[A_0]_n^{n-1}} = \left\{ \frac{[A_0]_2}{[A_0]_n} \right\}^{n-1}$$

Substituting the values, we get

$$\frac{50}{25} = \left(\frac{a/2}{a}\right)^{n-1} \text{ or } \frac{2}{1} = \left(\frac{1}{2}\right)^{n-1} = \left(\frac{2}{1}\right)^{1-n}$$

or
$$1 - n = 1$$
 or $n = 0$

Hence, the reaction is of zero order.



 $_{\rm are\,5\,hrs\,and\,15\,hrs}$ respectively. Calculate the average half-life $_{\rm for\,the\,decay}$ of A.

Solverage
$$t_{1/2} = \frac{1}{t} = \frac{t_1 \times t_2}{t_1 + t_2} = \frac{5 \times 15}{(5 + 15)} = \frac{75}{20} = 3.75 \text{ hrs}$$

4.9 PSEUDO MOLECULAR REACTIONS

4.9.1 PSEUDO UNIMOLECULAR REACTIONS WHEN O.R. = 1, BUT MOLECULARITY = 2

There are reactions in which more than one species is involved in the rate-determining step, but the order of the reaction is 1. Such reactions are known as pseudo unimolecular reactions or pseudo first order reactions and they involve solvent molecules or a catalyst as one of the reacting species. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning (t=0) and completion (t) of the reaction are given as inder.

The concentration of water does not get altered much during the course of the reaction. So in the rate equation

Rate =
$$k'$$
[CH₃COOC₂H₅] [H₂O]

The term $[H_2O]$ can be taken as constant. The equation, thus, becomes

Rate =
$$k[CH_3COOC_2H_5]$$

where $k = k'[H_2O]$

and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions. Thus, the reactions having molecularity ≥ 2 but the order of the reaction is 1 are called pseudo unimolecular reaction e.g.,

a. Hydrolysis of ester:

$$RCOOR' + H_2O \xrightarrow{H^{\oplus}} RCOOH + R'OH$$

$$\therefore Rate = k[Ester]^1 [H_2O]^0$$

$$\therefore$$
 OR = 1, but molecularity = 2

b. Inversion of cane sugar:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$$
Glucose Fructose

$$\therefore Rate = k[Sugar] [H_2O]^0$$

$$\therefore$$
 OR = 1, but molecularity = 2

c.
$$(CH_3CO)_2O + 2C_2H_5OH \longrightarrow 2CH_3COOC_2H_5 + H_2O$$

Acetic anhydride (Ethanol, excess) Ethyl acetate

$$\therefore \text{ Rate} = k \left[(\text{CH}_3\text{CO})_2\text{O} \right]^1 \left[\text{C}_2\text{H}_5\text{OH} \right]^0$$

$$\therefore$$
 OR = 1, but molecularity = 3

The concentration of the solvent (either H_2O or C_2H_5OH) being in excess and the amount used up in the course of reaction is negligible with the total, so that the concentration remains virtually constant and thus the reaction rate is not influenced by the solvent concentration in above examples.

Units of the rate constant (k') of a pseudo unimolecular reaction when molecularity is 2.

For first order reaction: Rate =
$$k[Ester]$$
 ...(i)

For pseudo first order reaction: Rate =
$$k'$$
[Ester] [H₂O] ...(ii)

Compare Eqs. (i) and (ii),

$$k[Ester] = k'[Ester] [H_2O]$$

$$\therefore k' = \frac{k(\text{for first order})}{[\text{H}_2\text{O}]} = \frac{t^{-1}}{\text{mol } L^{-1}} = L \text{ mol}^{-1} t^{-1}.$$

k' (for pseudo first order) = L mol⁻¹ t^{-1} .

Units of k' represents a second order reaction.

4.9.2 PSEUDO UNIMOLECULAR REACTION, WHEN O.R. = 1, BUT MOLECULARITY OF REACTION = 3

Example: Preparation of esters from anhydride and alcohol

$$\begin{array}{ccc}
O & O \\
\parallel & \parallel \\
RC - O - C - R & + & 2R' OH \longrightarrow 2RCOOR' + H_2O \\
& & (solvent)
\end{array}$$

[Solvent] remains nearly constant during the course of reaction

Units of k' of above type of reaction:

For 1st order reaction: Rate =
$$k \{(RCO)_2O\}$$
 ...(i)

For pseudo unimolecular reaction (molecularity = 3)

$$= k' [(RCO)_2O] [R'OH]^2$$
 ...(ii)

Compairing eq. (i) and (ii)

$$k[(RCO)_2O] = k'[(RCO)_2O] [R'OH]^2$$

$$k' = \frac{k \text{ (for 1st order)}}{[R'OH]^2} = \frac{t^{-1}}{\text{mol}^2 L^{-2}}$$

= L^2 mol⁻² t⁻¹ (Units of 3rd order reaction)

4.9.3 PSEUDO BIMOLECULAR REACTIONS WHEN REACTIONS HAVING MOLECULARITY \geq 3, BUT O.R. = 2

Example: Saponification of ester.

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Units of rate constant (k') of a pseudo bimolecular reaction when molecularity is 3.

For second order reaction : Rate =
$$k[Ester] [\overset{\circ}{O} H]$$
 ...(i)

For pseudo second order reaction : Rate =
$$k'$$
[Ester] $\stackrel{\circ}{[OH]}$ $[H_2O]$



Compare Eqs. (i) and (ii),

Compare Eqs. (f) and (a),
$$k[\text{Ester}] \stackrel{\circ}{[\text{OH}]} = k'[\text{Ester}] \stackrel{\circ}{[\text{OH}]} [\text{H}_2\text{O}]$$

$$k' = \frac{k(\text{for second order})}{[\text{H}_2\text{O}]}$$

$$= \frac{(\text{mol } \text{L}^{-1})^{1-n} t^{-1}}{(\text{mol } \text{L}^{-1})} \quad (\text{for } n = 2)$$

$$= \frac{(\text{mol } \text{L}^{-1})^{-1} t^{-1}}{(\text{mol } \text{L}^{-1})}$$

$$= \text{mol}^{-2} \text{L}^2 t^{-1}$$

.: k' (for pseudo second order) = $L^2 \text{ mol}^{-2} t^{-1}$ Units of k' represent a third order reaction.

4.9.4 PSEUDO BIMOLECULAR REACTION WHEN O.R. = 2, BUT MOLECULARITY OF REACTION > 3 OR 4

Example: Hypothetical reaction

$$A + B + 2C$$
 (solvent) $\longrightarrow P + Q$

[Solvent] remains nearly constant during the course of reaction.

Unit of k' of above type of reaction:

For
$$2^{nd}$$
 order reaction: Rate = k [A] [B] ...(i)

For pseudo bimolecular reaction (molecularity = 4)

$$= k' [A] [B] [C]^2_{\text{solvent}} \qquad ...(ii)$$

Comparing eq. (i) and (ii)

$$k[A][B] = k'[A][B][C]^2$$

$$k' = \frac{k(\text{for 2nd order})}{[C]^2} = \frac{L \text{ mol}^{-1} \text{ s}^{-1}}{\text{mol}^2 \text{ L}^{-2}}$$

= L^3 mol⁻³ t⁻¹ (Units of 4th order reaction)

ILLUSTRATION 4.105

The hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against NaOH. The concentration of ester at different times is given below:

t (min)	0	30	60	90
C (Mol L ⁻¹)	0.8500	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction, as the concentration of water remains nearly constant (55 mol L^{-1}) during the course of the reaction. What is the value of k' in the equation?

$$Rate = k'[CH_3COOCH_3][H_2O]$$

Sol. For a pseudo first order reaction, the reaction should be first order w.r.t. ester when $[H_2O]$ is constant. The rate constant k for pseudo first order reaction is:

For first order reaction: rate = $k [CH_3COOCH_3]$...(i)

For pseudo first order reaction:

Rate =
$$k'$$
 [CH₃COOCH₃] [H₂O] ...(ii)

Compare Eqs. (i) and (ii),

$$k [CH3COOCH3] = k' [CH3COOCH3] [H2O]$$

$$\therefore k = k' [H_2O]$$

Thus rate constant k for pseudo first order reaction j_{s} .

$$k = \frac{2.303}{t} \log \frac{c_0}{c_t}$$
, where c_0 is the initial concentration of ester left after time t .

Thus, when $t = 30$ min

$$k = \frac{2.3}{30} \log \left(\frac{0.85}{0.8004} \right) = 2.004 \times 10^{-3} \,\mathrm{min}^{-1}$$

When t = 60 min

$$k = \frac{2.3}{60} \log \left(\frac{0.85}{0.7538} \right) = 2.002 \times 10^{-3} \,\mathrm{min}^{-1}$$

When t = 90 min

$$k = \frac{2.3}{90} \log \left(\frac{0.85}{0.7096} \right) = 2.005 \times 10^{-3} \,\mathrm{min}^{-1}$$

It can be seen that $k'[H_2O]$ is constant and equal to $2.004 \times 10^{-3} \, \text{min}^{-1}$ and hence it is pseudo first order reaction. Thus, k' can be determined as follows:

$$k'[H_2O] = 2.004 \times 10^{-3} \text{ min}^{-1}$$

$$k'$$
 (55 mol L⁻¹) = 2.004 × 10⁻³ min⁻¹

$$\therefore k' = \frac{2.004 \times 10^{-3} \text{ min}^{-1}}{55 \text{ mol L}^{-1}} = 3.64 \times 10^{-5} \text{ mol}^{-1} \text{ L min}^{-1}$$

Note: Units of k' represent second order reaction.

ILLUSTRATION 4.106

Pseudo first order rate for the reaction

$$A + B \longrightarrow P$$

when studied in 0.1 M of B is given by

$$-\frac{d[A]}{dt} = -k[A]$$

where $k = 1.85 \times 10^4 \text{ s}^{-1}$. Calculate the value of second order rate constant.

Sol.
$$A + B \longrightarrow P$$

$$-\frac{d[A]}{dt} = k[A]$$

$$d[A] = k[A]$$

$$-\frac{d[A]}{dt} = 1.85 \times 10^4 \times [A]$$

Assuming the reaction to be of second order.

$$-\frac{d[A]}{dt} = k'[A][B]$$

$$-\frac{d[\mathbf{A}]}{dt} = k'[\mathbf{A}][0.1]$$

...(ii)

...(i)

Dividing Eq. (i) by Eq. (ii), we get

$$1 = \frac{1.85 \times 10^4}{k'[0.1]}$$

$$k' = 1.85 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$$

TYPICAL FIRST ORDER GAS PHASE REACTIONS

whider a typical first order gas phase reaction:

$$\underset{A(g)}{\text{A(g)}} \longrightarrow B(g) + C(g)$$

Att = 0

At time t

Let P_0 be the initial pressure of A and P_t is the total pressure The integrated rate equation for such a reaction can be derived as:

Total pressure $(P_i) = P_A + P_B + P_C$ (pressure units), where $p_{\rm g}$, $p_{\rm g}$ and $p_{\rm C}$ are the partial pressures of A, B, and C, respectively. If x atmosphere be the decrease in the pressure of A at time rand one mole each of B and C is being formed, then increase in be pressure of B and C will also be x atm each.

$$\begin{array}{ccccc} A(g) & \longrightarrow & B(g) & + & C(g) \\ P_0 \text{ atm} & & 0 \text{ atm} & & 0 \text{ atm} \\ (P_0 - x) \text{ atm} & & x \text{ atm} & & x \text{ atm} \end{array}$$

where P_0 is the initial pressure at time t=0.

$$P_{t} = (P_{0} - x) + x + x = P_{0} + x$$

$$x = (P_{t} - P_{0})$$
where $P_{A} = P_{0} - x = P_{0} - (P_{t} - P_{0})$

$$= 2p_{0} - p_{t}$$

$$k = \left(\frac{2.303}{t}\right) \left(\log \frac{P_{0}}{P_{A}}\right)$$

$$= \frac{2.303}{t} \log \frac{P_0}{(2P_0 - P_t)} \qquad ...(i)$$

ILLUSTRATION 4.107

The following data were obtained during the first order thermal decomposition of N₂O₅ (g) at constant volume.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

No.	Time (s)	Total pressure (atm	
1.	0	0.5	
11.	100	0.512	

Calculate the rate constant.

Let the pressure of $N_2O_5(g)$ decreases by 2x atm. As 2 mol of N_2O_5 decompose to give 2 mol of $N_2O_4(g)$ and $1 \text{ mol of } O_2(g)$, the pressure of $N_2O_4(g)$ increases by 2x atm and that of $O_2(g)$ increases by x atm.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$
When $t = 0$ 0.5 atm 0 atm 0 atm
At time t (0.5 - 2x) atm 2x atm x atm

Total pressure
$$(p_i) = p_{(N_2O_5)} + p_{(N_2O_4)} + p_{(O_2)}$$

= $(0.5 - 2x) + 2x + x = 0.5 + x$

$$x = p_i - 0.5$$

$$p_{(N_2O_5)} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm

$$p_{A(N_2O_5)} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Using Eq. (i) above,

$$= \frac{2.303}{t} \log \left(\frac{p_0 (N_2 O_5)}{p_A (N_2 O_5)} \right)$$

$$=\frac{2.303}{100 \text{ s}} \log \left(\frac{0.5 \text{ atm}}{0.476 \text{ atm}} \right)$$

$$= \frac{2.303}{100 \,\mathrm{s}} \times 0.0216 = 4.98 \times 10^{-4} \,\mathrm{s}^{-1}$$

ILLUSTRATION 4.108

A gaseous reaction

 $A_2(g) \longrightarrow B(g) + \frac{1}{2} C(g)$ shows increase in pressure from 100 mm to 120 mm in 5 min. What is the rate of disappearance of A_2 ?

Sol. $A_2(g) \longrightarrow B(g) + \frac{1}{2}C(g)$ At eq

Total pressure =
$$P - x + x + \frac{x}{2} = P + \frac{x}{2}$$

Initial pressure (P) = 100 mm

Final pressure = Total pressure = 120 mm

$$\therefore P + \frac{x}{2} = 120$$

$$100 + \frac{x}{2} = 120$$

$$x = 40 \text{ mm}$$

$$\therefore \frac{-d[A_2]}{dt} = \frac{40}{5} = 8 \text{ mm min}^{-1}$$

ILLUSTRATION 4.109

Azoisopropane decomposes according to the reaction:

$$(CH_3)_2CHN = NCH(CH_3)_2(g) \xrightarrow{250-290^{\circ}C} N_2(g) + C_6H_{14}(g)$$

It is found to be a first order reaction. If the initial pressure is P_0 and pressure of the mixture at time $+i$ (P) in the same of the mixture at time $+i$ (P) in the same of the mixture at time $+i$ (P) in the same of the mixture at time $+i$ (P) in the same of the s

 P_0 and pressure of the mixture at time t is (P_t) , then the rate constant (k) would be

a.
$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_0}$$

b.
$$k = \frac{2.303}{t} \log \frac{P_0 - P_t}{P_0}$$

$$c. \ k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P_0}$$

d.
$$k = \frac{2.303}{t} \log \frac{2P_0}{2P_0 - P_0}$$

Solve a.
$$(CH_3)_2 CH = NCH(CH_3)_2 \longrightarrow N_2 + C_6 H_{14}$$

$$t = 0 \qquad P_0 \qquad 0 \qquad 0$$

$$t = t \qquad P_0 - x \qquad x \qquad x$$

$$P_t = P_0 - x + x + x = P_0 + x$$

$$x = (P_t - P_0)$$

$$(a - x) = (P_0 - x) = P_0 - (P_t - P_0)$$

$$= 2P_0 - P_t$$

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$= \frac{2.303}{t} \log \frac{(P_0)}{(2P_0 - P_t)}$$

ILLUSTRATION 4.110

For a reaction

$$\text{CH}_3\text{OCH}_3(g) \longrightarrow \text{CH}_4(g) + \text{H}_2(g) + \text{CO}(g)$$
 at 750 K, the rate constant is $6.72 \times 10^{-3} \text{ min}^{-1}$. Starting with a pressure of 400 mm of Hg at this temperature in a closed container, how many minutes would it take for the pressure in the container to become 760 mm Hg?

Sol.
$$CH_3OCH_3 \longrightarrow CH_4 + H_2 + CO$$

 $t = 0$ 400 0 0 0
 $t = t$ (400 - P) P P P
 $P_t \propto 400 - P + P + P + P$
 $\propto 400 + 2P \propto 760$
 $2P \propto 360$
 $P \propto 180$
 $t = \frac{2.303}{6.72 \times 10^{-3}} \log \frac{400}{400 - 180} = 89.1 \min$

ILLUSTRATION 4.111

Following data were obtained during the thermal decomposition of sulphuryl chloride at constant volume and 285°C.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

L L				
Time (s)	0	240	600	
Pressure (torr)	180	244	302	

Show that it is first order reaction.

Sol.
$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$
Initial $180 \qquad 0 \qquad 0$
At time $t \qquad 180 - x \qquad x \qquad x$

$$P_{\text{total}} = 180 - x + x + x = 180 + x$$
a. $t = 240 \text{ s}, P_t = 244$

$$\therefore 180 + x = 244 \Rightarrow x = 64$$

$$k = \frac{2.303}{240} \log \frac{a}{a - x} = \frac{2.303}{240} \log \frac{180}{180 - 64}$$

$$= \frac{2.303}{240} \times 0.1909 = 0.00183 \text{ s}^{-1}$$

b.
$$t = 600 \text{ s},$$
 $P_t = 302 \text{ torr}$
 $180 + x = 302,$ $x = 122 \text{ torr}$
 $k = \frac{2.303}{600} \log \frac{180}{180 - 122}$
 $= \frac{2.303}{600} \times 0.4918 = 0.0018 \text{ s}^{-1}$

Since the value of k is constant and hence first order reaction.

ILLUSTRATION 4.112

Some PH_3 is introduced into a flask at 600° C containing inert gas. PH_3 decomposes to give $P_4(g)$ and $H_2(g)$. The total pressure as a function of time is given below.

Time (s)	0	60	120	00
Pressure (mm) (total)	262.4	272.9	275.53	276.4

Find the order and half life.

Sol.
$$4PH_{3}(g) \longrightarrow P_{4}(g) + 6H_{2}(g)$$
Or
$$PH_{3}(g) \longrightarrow \frac{1}{4}P_{4}(g) + \frac{3}{2}H_{2}(g)$$
Initial $a = 0 = 0$
Final $a - x = \frac{x}{4} + \frac{3}{2}x$

$$P_{t} \propto a - x + \frac{x}{4} + \frac{3}{2}x$$

$$P_{t} \propto a + \frac{3}{4}x$$
a. When $t = 0$, $a \propto 262.4$

$$a + \frac{3}{4}x \propto 272.9$$

$$\frac{3}{4}x \propto 272.9 - 262.4$$

$$x \propto \frac{4}{3} \times 10.5 = \frac{42}{3} = 14$$

$$k = \frac{2.303}{60} \log \frac{262.4}{262.4 - 14}$$

$$= \frac{2.303}{60} \log \frac{262.4}{248.4}$$

$$= \frac{2.303}{60} \times 0.0238 = 0.0007$$
b. When $t = 120$ s
$$a \propto 262.4$$

$$\therefore a + \frac{3}{4}x \propto 275.53$$

$$\frac{3}{4}x \propto 275.53 - 262.4$$

 $=\frac{2.303}{60}\log(1.056)$

$$x \propto \frac{4}{3} \times 13.13 \propto 17.5$$

$$k = \frac{2.303}{120} \log \frac{262.4}{262.4 - 17.5}$$

$$= \frac{2.303}{120} \log \frac{262.4}{244.9}$$

$$= \frac{2.303}{120} \log 1.07$$

$$= \frac{2.303}{120} \times 0.029$$

$$= 0.0005$$
Average $k = \frac{0.0007 + 0.0005}{2} = 0.0006$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0007} = 990 \text{ s}$$

ILLUSTRATION 4.113

Arsine decomposes on heating according to the equation $2AsH_3(g) \longrightarrow 2As(s) + 3H_2(g)$. The decomposition was studied at constant temperature and constant volume by measuring the total pressure at various intervals of time.

Time (min)	0	5	7.5	10	
Total pressure (atm)	1	1.09	1.13	1.16	

Assume it to be a first order reaction, calculate the specific rate constant and half life of the reaction.

Note: Here As is in solid form

$AsH_3(g) \longrightarrow As(s) + \frac{3}{2}H_2(g)$ Initial $1 \qquad 0 \qquad 0$ At time $t \qquad 1-x \qquad 0 \qquad \frac{3}{2}x$

a.
$$1-x+\frac{3}{2}x \propto 1.09 \implies x \propto 0.18$$

$$\therefore k = \frac{2.303}{5} \log \frac{1}{1-0.18} = \frac{2.303}{5} \times 0.084$$

$$= 0.04 \text{ min}^{-1}$$

b.
$$1-x+\frac{3}{2}x \propto 1.13 \implies x \propto 0.26$$

$$k = \frac{2.303}{7.5} \log \frac{1}{1-0.26}$$

$$= \frac{2.303}{7.5} \log \frac{1}{0.74}$$

$$= \frac{2.303}{7.5} \times 0.1306 = 0.0401 \text{ min}^{-1}$$

c.
$$1 - x + \frac{3}{2}x \propto 1.16 \implies x \propto 0.32$$

$$k = \frac{2.303}{10} \log \frac{1}{1 - 0.32}$$

$$= \frac{2.303}{10} \log \frac{1}{0.68}$$

$$= \frac{2.303}{10} \times 0.1676 = 0.039 \text{ min}^{-1}$$
Mean value of $k = \frac{0.04 + 0.0401 + 0.039}{3}$

$$= 0.0397 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0397} = 17.46 \text{ min}$$

ILLUSTRATION 4.114

The following first order order reaction takes places at 410 K:

$$2CO(g) \longrightarrow CO_2(g) + C(s)$$

The total pressure at the end of 401 s after starting with pure CO(g) is found to be 0.313 atm. At the time the reaction is 100% complete, the total pressure is found to be 0.1645 atm. Find

- a. The rate constant of the reaction.
- b. The pressure of CO after 401 s.

Note: Here C is in solid form.

Sol. a.
$$2\text{CO}(g) \longrightarrow \text{CO}_2(g) + \text{C}(s)$$
or
 $\text{CO}(g) \longrightarrow \frac{1}{2}\text{CO}_2(g) + \frac{1}{2}\text{C}(s)$
Initial $a = 0 = 0$
At time $t = a - x = \frac{x}{2} = 0$

[100%] 0
$$\frac{a}{2}$$
 — decomposition

$$\frac{a}{2} = 0.1645 \Rightarrow a = 0.329$$

Total moles at time t

$$a - x + \frac{x}{2} = 0.313$$

$$\therefore x = 0.032$$

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$= \frac{2.303}{401} \log \frac{0.329}{0.329 - 0.032}$$

$$= \frac{2.303}{401} \log \frac{0.329}{0.297}$$

$$= \frac{2.303}{401} \times 0.0443 = 2.5 \times 10^{-4} \text{ s}^{-1}$$

b. Pressure of CO after 401 s is
$$a - x$$

= 0.329 - 0.320 = 0.297

4.11 ANALYSIS OF SOME IMPORTANT FIRST ORDER REACTIONS

4.11.1 DIRECT OR INDIRECT ESTIMATION OF **REACTANTS**

Sometimes volumes of reagents are given in volumetric analysis (when one of the reactant is estimated directly or indirectly, i.e., when V_{∞} is not given).

For example, in the decomposition of H_2O_2 , H_2O_2 is titrated against KMnO₄ or K₂Cr₂O₇ in acidic medium at different intervals of time. Then, the formula used is:

$$k = \frac{2.303}{t} \log \left(\frac{V_0}{V_t} \right)$$

where V_0 = Volume of reagent used at zero time

 V_{i} = Volume of reagent used at time t

 V_{∞} = Volume of reagent used at infinite time, or when the reaction is 100% complete.

Let us take an example of decomposition of hydrogen peroxide $(H_2O_2).$

$$2H_2O_2(1) \longrightarrow 2H_2O(1) + O_2(g)$$

The rate of this first order reaction is measured by titrating a fixed volume of H₂O₂ (undecomposed) against a standard solution of KMnO₄. Here KMnO₄ acts as oxidizing agent and H₂O₂ acts as reducing agent. The volumes of KMnO₄ used for H₂O₂ after regular intervals of time are as follows.

Time instants	t = 0	t_1	t_2	t_3	t_4	t ₅
Vol of KMnO ₄	V_0	V_1	V_2	V_3	V_4	V_5

Volume of KMnO₄ at t = 0 corresponds to volume of H₂O₂ initially present.

$$\Rightarrow c_0 \propto V_0$$

Volume of KMnO₄ at time instant $t_1, t_2, t_3,...$ corresponds to volume of H_2O_2 remaining after $t_1, t_2, t_3,...$

$$\Rightarrow c_t \propto V_t$$

Now it being a first order reaction, follows first order kinetics, So

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Now using the above expression, if we calculate the values of k for different intervals $t_1, t_2, ...$ (for actual numerical data), the values of k should be same if the reaction follows first order kinetics.

4.11.2 DIRECT OR INDIRECT ESTIMATION OF **PRODUCTS**

Consider a condition when one of the product is estimated directly or indirectly, i.e., when V_0 is not given.

For example, in the decomposition of NH₄NO₂, the volume of N₂ is directly measured at different intervals of time. Then, the formula used is

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_{t}}$$

An example is the decompostion of ammonium nitrite (NH_4NO_2) and benzene diazonium chloride $(C_6H_5N = NCI)$

$$NH_4NO_2(s) \longrightarrow 2H_2O(l) + N_2(g)$$

$$C_6H_5 - N = N - C1 \longrightarrow C_6H_5 - C1 + N_2(g)$$

The rate of both the reactions is studied (measured) in similar manner. The volume of nitrogen (N₂) is collected after a regular interval of times as follows:

Time instants	t = 0	t_1	t_2	t_3	t_4	t_{∞}
Vol of N ₂	0	V_1	V_2	V_3	V_4	V

At t = 0, clearly the volume of $N_2 = 0$.

Time instant $t = \infty$ means the end of a reaction, i.e., when whole of NH_4NO_2 or C_6H_5 —N = N—C1 is decomposed.

$$\Rightarrow$$
 At $t = \infty$, V_{∞} corresponds to the initial volume of NH_4NO_2 or $C_6H_5 - N = N - Cl$.

(Note that the ratio of stoichiometric coefficient for both N. NH_4NO_2 or N_2 : $C_6H_5N = NC1$ is 1 : 1)

$$\Rightarrow$$
 $c_0 \propto V_{\infty}$

At $t = t_1, t_2, t_3, \dots$ the volume of N₂ corresponds to the concentration of product formed, i.e., equal to x.

$$\Rightarrow x \propto V_{\infty}$$

$$\Rightarrow$$
 $c_0 - x \propto V_{\infty} - V_t$

Hence, from first order kinetic,

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_{t}}$$

4.11.3 HYDROLYSIS OF ESTERS (CH₃COOR') IN **ACIDIC MEDIUM**

$$CH_3COOR'$$
 (Ester) + H_2O + $HC1$ (H^{\oplus}) \longrightarrow CH_3COOH
+ C_2H_5OH

The reaction rate is measured by titrating the acid (CH₃COOH) produced against a standard alkali solution. Note that when a test sample is prepared from the reacting mixture, there are two acids: one is mineral acid H^{\oplus} (HCl or any other) and second is CH_3COOH produced. So the volume of alkali used gives the titration value for both acids. The data is collected in the following manner:

Time instants	t = 0	t_1	t_2	t_3	t_4 t_{∞}
Vol of NaOH	V_0	V_1	V_2	V_3	V_4 V_{∞}

a. When V_0 is given

At t = 0, V_0 is the volume NaOH used to neutralize the mineral acid. mineral acid present (H^{\oplus}) being used as catalyst. (At $t = \emptyset$, no CH₃CHOOH is yet produced)

At $t = \infty$ (i.e., at the end of hydrolysis), V_{∞} is the volume of NeOVI of NaOH used to neutralize whole of CH₃COOH plus the volume of HCl present. At $t = \infty$, the volume of CH_3COO^H corresponds to the volume of ester taken initially.

$$\Rightarrow c_0 \propto V_{\infty} - V_0$$
 (as $V_0 \equiv \text{volume of HCl}$)

At $t = t_1, t_2, t_3, ..., V_1, V_2, V_3, ...$ correspond to the volume of HCl plus the volume of HCl plus the volume of CH₃COOH being produced.

$$\Rightarrow x \propto V_t - V_0$$

$$\Rightarrow c_0 - x \propto (V_\infty - V_0) - (V_t - V_0)$$

$$\Rightarrow c_0 - x \propto V_\infty - V_t$$

Hence, from the first order kinetics, it follows:

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

$_{ m b.}$ When $V_{ m 0}$ is not given

Let
$$[V_{\infty} - V_0 = c_0]$$
 and $V_{\infty} - V_t = c_t$

When $t = t_1$, then

$$k = \frac{2.303}{t_1} \log \frac{c_0}{c_{t_1}} \qquad ...(i)$$

Similarly, when $t = t_2$

$$k = \frac{2.303}{t_2} \log \frac{c_0}{c_{t_2}} \qquad ...(ii)$$

Operating Eq. (i) - Eq. (ii), we get

$$k(t_1 - t_2) = 2.303 \log \frac{c_{t_2}}{c_{t_1}}$$
or $k = \frac{2.303}{(t_1 - t_2)} \log \frac{c_{t_2}}{c_{t_1}}$...(iii)

Similarly, when $t = t_3$ and so on, we get

$$k = \frac{2.303}{(t_1 - t_3)} \log \frac{c_{t_3}}{c_{t_1}} \qquad \dots (iv)$$

4.11.4 INVERSION OF CANE SUGAR ($C_{12}H_{22}O_{11}$)

$$C_{12}H_{22}O_{11} + H_2O + H^{\oplus} \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
(Glucose) (Fructose)

The rate is measured by measuring the change in the angle of rotation (optical activity) by a polarimeter. Sucrose is *dextro-rotatory*, glucose is *dextro rotatory*, and fructose is *leavo-rotatory*. The change produced in rotatory power in time t gives a measure of x, the quantity of sucrose decomposed at that time. The total change in the rotatory power produced at the end of reaction gives the measure of c_0 , the initial concentration of sucrose.

If r_0 , r_p and r_{∞} represent rotations at the start of reaction, after time t, and at the end of reaction, respectively, then

$$\Rightarrow c_0 \propto r_0 - r_\infty$$
 and $x \propto r_0 - r_t \Rightarrow c_0 - x \propto r_t - t_\infty$

$$\Rightarrow k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

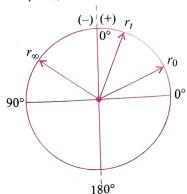


Fig. 4.11 Change of optical rotation from (+) to (-)

ILLUSTRATION 4.115

The following data were reported for the decomposition of N_2O_5 in CCl₄ at 303 K:

Time (min)	120	160	200	240	00 -
Vol of O ₂ (mL)	37.70	45.85	52.67	58.34	84.35

Show that the reaction is of the first order and calculate the rate constant.

Note: This is an example of direct-estimation of product, i.e., O2.

Sol.
$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_{\infty}}$$

a.
$$k = \frac{2.303}{120} \log \frac{84.35}{84.35 - 37.70}$$

= $\frac{2.303}{120} \log \frac{84.35}{46.65}$
= $\frac{2.303}{120} \times 0.2572 = 0.0049 \text{ min}^{-1}$

b.
$$k = \frac{2.303}{160} \log \frac{84.35}{84.35 - 45.85} = 0.0049 \text{ min}^{-1}$$

c.
$$k = \frac{2.303}{200} \log \frac{84.35}{84.35 - 52.67} = 0.0049 \text{ min}^{-1}$$

d.
$$k = \frac{2.303}{240} \log \frac{84.35}{84.35 - 58.34} = 0.0049 \text{ min}^{-1}$$

The value of *k* is constant. Hence, first order reaction.

ILLUSTRATION 4.116

In an experiment on the decomposition of an aqueous NH₄NO₂ at a certain temperature, the volume of nitrogen gas collected at different intervals of time was as follows:

Time (s)	1190	2300	∞
Vol of N ₂ (mL)	5.00	7.30	9.50

Show how the above data illustrate that the reaction is of first order.

Note: This is an example of direct-estimation of product, i.e., N₂.

Sol.
$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

a.
$$k = \frac{2.303}{1190} \log \frac{9.50}{9.50 - 5.0}$$

= $\frac{2.303}{1190} \log \frac{9.50}{4.5}$
= $\frac{2.303}{1190} \times 0.32 = 0.0006 \text{ s}^{-1}$

b.
$$k = \frac{2.303}{2300} \log \frac{9.50}{9.50 - 7.30}$$

$$= \frac{2.303}{2300} \times 0.635 = 0.0006 \,\mathrm{s}^{-1}$$

The value of k is constant. Hence, first order reaction.

ILLUSTRATION 4.117

In the dehydration of oxalic acid by cone H₂SO₄

$$(COOH)_2 \longrightarrow CO + CO_2 + H_2O$$

2 mL of the solution was withdrawn at different times and titrated against 0.1 N KMnO₄ solution. Show that the reaction is of first order

is of first order.			Address of the second s	
Time (mins)	0	300	450	600
Vol of KMnO ₄	22.0	17.0	15.0	13.4
used (mL)				

Note: This is an example of indirect estimation of reactant, i.e., titration of oxalic acid by KMnO₄.

Sol.
$$(COOH)_2 \longrightarrow CO + CO_2 + H_2O$$

$$k = \frac{2.303}{t} \log \frac{V_0}{V_*}$$

a.
$$k = \frac{2.303}{300} \log \frac{22}{17}$$

= $\frac{2.303 \times 0.119}{300} = 0.00085 \text{ min}^{-1}$

b.
$$k = \frac{2.303}{450} \log \frac{22}{15} = 0.00085 \text{ min}^{-1}$$

c.
$$k = \frac{2.303}{600} \log \frac{22}{13.4} = 0.00085 \text{ min}^{-1}$$

The value of k is constant. Hence, first order reaction.

ILLUSTRATION 4.118

Methyl acetate was subjected to hydrolysis in N-HCl at 298 K. 5 mL of the mixture is withdrawn at different intervals and titrated with about N/8 NaOH. The following results were obtained:

		tuilleu.			
Time (min)	0	25	40	61	90
Vol of alkali	19.24	24.20	26.60	29.50*	42.1
used (mL)					12.1

Show that the reaction is of first order.

Sol.
$$CH_3COOCH_3 + H_2O \xrightarrow{H^{\oplus}} CH_3COOH + CH_3OH$$

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

a.
$$k = \frac{2.303}{25} \log \frac{42.1 - 19.24}{42.1 - 24.2}$$

= $\frac{2.303}{25} \log \frac{22.86}{17.9}$
= $\frac{2.303}{25} \times 0.106 = 0.0097 \text{ min}^{-1}$

b.
$$k = \frac{2.303}{40} \log \frac{42.1 - 19.24}{42.1 - 26.6}$$

= $\frac{2.303}{40} \times 0.1687 = 0.0097 \text{ min}^{-1}$

c.
$$k = \frac{2.303}{61} \log \frac{42.1 - 19.24}{42.1 - 29.5} = 0.0097 \text{ min}^{-1}$$

The value of k is constant. Hence, first order reaction.

ILLUSTRATION 4.119

A 20% solution of cane sugar having dextrorotation of 34.50 inverted by 0.5 N lactic acid to at 298 K. The rotations determined are as follows:

Time (min)	0	14.55	111.36	00
Rotation	34.50	31.10	13.98	-10.77

Show that the inversion of sugar is a unimolecular reaction.

Sol.
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$k = \frac{2.303}{t} \log \frac{r_0 - r_{\infty}}{r_t - r_{\infty}}$$

a.
$$k = \frac{2.303}{14.55} \log \frac{34.50 - (-10.77)}{31.1 - (-10.77)}$$

= $\frac{2.303}{14.55} \log \frac{45.27}{41.87}$
= $\frac{2.303 \times 0.0339}{14.55} = 0.0053 \text{ min}^{-1}$

b.
$$k = \frac{2.303}{111.36} \log \frac{34.50 - (-10.77)}{13.98 - (-10.77)}$$

= $\frac{2.303}{111.36} \log \frac{45.27}{24.75} = \frac{2.303 \times 0.262}{111.36} = 0.054 \text{ min}^{-1}$

The value of k is constant. Hence, first order reaction.

ILLUSTRATION 4.120

Methyl acetate is hydrolyzed with 0.1 N HCl at 25°C. 5 mL of the reacting mixture is withdrawn at various time intervals and is quickly titrated with 1.0 N NaOH. The volumes of NaOH consumed are as follows:

Time (s):	339	1242	2745	4546	00
Vol of NaOH	26,34	27.80	29.70	31.81	39.81
(mL)		27.00	29.70	31.01	37.0

Show that the hydrolysis is a first order reaction. Also find the rate constant (k).

Sol. For ester hydrolysis, equation
$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

Since V_0 is not given

Let
$$V_{\infty} - V_0 = c_0$$
 and $V_{\infty} - V_t = c_t$.

When $t = t_1$

$$k = \frac{2.303}{t_1} \log \frac{c_0}{c_{t_1}} \qquad ...(i)$$

Similarly, when
$$t = t_2$$

$$k = \frac{2.303}{t_2} \log \frac{c_0}{c_{t_2}} \qquad ...(ii)$$

Operating Eq. (i) Eq. (ii), we get

$$k(t_1 - t_2) = 2.303 \log \frac{c_{t_2}}{c_{t_1}}$$

or
$$k = \frac{2.303}{(t_1 - t_2)} \log \frac{c_{t_2}}{c_{t_1}} \qquad ...(iii)$$

Now find c_t .

339 s	1242 s	2745 s	4546 s
39.81 - 26.3	4 39.81 – 27.80	39.81 - 29.70	39.81 – 31.81
$\frac{c_t}{=V_{\infty}-V_t} = 13.47 \text{ mL}$	ter the first party of the first terms of the first	= 10.11 mL	

and
$$t_1 - t_2 = 339 - 1242 = -903 \text{ s}$$

 $t_1 - t_3 = 339 - 2745 = -2406 \text{ s}$
 $t_1 - t_4 = 339 - 4546 = -4207 \text{ s}$

Using relation given in Eq. (iii),

$$k_1 = \frac{2.303}{-903} \log \frac{12.0}{13.47} = -0.0025 \times \log (0.89)$$

$$= -0.0025 \times -0.0506 = 1.27 \times 10^{-4} \text{ s}^{-1}$$

$$k_2 = \frac{2.303}{-2406} \log \frac{10.11}{13.47} = -0.00095 \times \log (0.75)$$

$$= -0.00095 \times -0.1249 = 1.19 \times 10^{-4} \text{ s}^{-1}$$

$$k_3 = \frac{2.303}{-4207} \log \frac{8.0}{13.47} = -0.00054 \times \log (0.59)$$

$$= -0.00054 \times -0.2291 = 1.23 \times 10^{-4} \text{ s}^{-1}$$

$$k_{\text{average}} = 1.23 \times 10^{-4} \text{ s}^{-1}$$

ILLUSTRATION 4.121

The first order reaction:

Sucrose — Glucose + Fructose takes place at 308 K in 0.5 N HCl. At time zero the initial total rotation of the mixture is 32.4°. After 10 min, the total rotation is 28.8°. If the rotation of sucrose per mole is 85°, that of glucose is 7.4°, and of fructose is -86.04°, calculate the half life of the reaction.

Let r_1, r_2, r_3 be rotation per mole of sucrose, glucose, and fructose, respectively.

Sucrose
$$\longrightarrow$$
 Glucose + Fructose
initial a 0 0
after time t $a-x$ x x

$$ar_1 = 32.4 \Rightarrow a = \frac{32.4}{85} = 0.38$$

$$(a-x)r_1 + xr_2 + xr_3 = 28.8$$

$$x (r_2 + r_3 - r_1) + ar_1 = 28.8$$

$$x(r_2 + r_3 - r_1) = 28.8 - 32.4 = -3.6$$

$$x(7.4 - 86.04 - 85) = -3.6$$

$$x = 0.022$$

$$k = \frac{2.3}{10} \log \left(\frac{0.38}{0.38 - 0.022} \right)$$

$$= 5.9 \times 10^{-3} \text{ min}^{-1}$$

$$\therefore t_{1/2} = \frac{0.693}{5.9 \times 10^{-3}} = 116.9 \text{ min}$$

ILLUSTRATION 4.122

In the acid hydrolysis reaction $A + H_2O + H^{\oplus} \longrightarrow Product$, where $[H^{\oplus}] = 0.1$ mol dm⁻³ and H_2O is present in large excess, the apparent rate constant is 1.5×10^{-5} s⁻¹. Calculate the true rate constant.

Sol.
$$r = \frac{-d[A]}{dt} = k[A] [H_2O] [H^{\oplus}]$$

Since $[H^{\oplus}]$ is essentially constant (because the catalyst is regenerated and $[H_2O]>>[A]$)

$$\therefore r = k_{\text{app}} [A], \text{ where } k_{\text{app}} = k [H_2O] [H^{\oplus}]$$

$$k = \frac{k_{\rm app}}{[{\rm H_2O}][{\rm H}^{\oplus}]}$$

 $[H^{\oplus}] = 0.1 \text{ mol dm}^{-3}$

$$[H_2O] = \frac{1000}{18} = 55.6 \text{ mol dm}^{-3}$$

Hence,
$$k = \frac{1.5 \times 10^{-5} \text{ s}^{-1}}{(55.6 \text{ mol dm}^{-3}) (0.1 \text{ mol dm}^{-3})}$$

= 2.7 × 10⁻⁶ dm⁶ mol⁻² s⁻¹
= 2.7 × 10⁻⁶ L² mol⁻² s⁻¹

ILLUSTRATION 4.123

Inversion of sucrose is studied by measuring the angle of rotation at any time t.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(Sucrose) (Glucose) (Fructose)

It is found that

 $(r_{\infty} - r_0) \propto a$ and $(r_{\infty} - r_t) \propto (a - x)$, where r_0 , r_t , and r_{∞} are the angle of rotation at the start, at the time t, and at the end of the reaction, respectively. From the following values calculate the rate constant and the time at which the solution is optically inactive.

Time (min)	0.0	46.0	∞
Rotation of polarized	24.1	10.0	-10.7
light (degree)			

Sol. When have been given

$$r_0 = 24.1^\circ, r_t = 10^\circ, r_\infty = -10.7^\circ$$

Thus, $a = (r_\infty - r_0) = -10.7 - 24.1 = -34.8^\circ$

$$(a-x) = (r_{\infty} - r_{t}) = -10.7 - 10.0 = -20.7$$

$$\therefore k = \frac{2.303}{46} \log \left(\frac{-34.8}{-20.7} \right) = 0.011 \,\mathrm{min}^{-1}$$

Solution is optically inactive when $r_t = 0$ after time t

Thus,
$$r_{\infty} - r_0 = -34.8^{\circ}$$
 and $r_{\infty} - r_t = -10.7^{\circ}$

Thus,
$$0.011 = \frac{2.303}{t} \log \left(\frac{-34.8}{-10.7} \right)$$
.

This gives t = 107.2 min.

CONCEPT APPLICATION EXERCISE 4.3

- 1. A first order reaction is 40% complete in 50 min. In how much time will the reaction be 80% complete?
- 2. The decomposition of N₂O₅ in CCl₄ solution follows the first order rate law. The concentration of N₂O₅ measured at different time intervals are given below:

Time in seconds (t)	7.15						
$[N_2O_5]$ (mol L ⁻¹)	5.5	5.0	4.8	4.0	3.4	2.4	1.6

Calculate the rate constant at t = 410 s and t = 1130 s. What do these results show?

- 3. A first order reaction is 20% complete in 10 min. Calculate the time taken for the reaction to go to 80% completion.
- **4.** The decompostion of N_2O_5 in CCl_4 at $45^{\circ}C$

$$2N_2O_5 \xrightarrow{CCl_4} 4NO_2 + O_2$$

is first order reaction with $k=6.32\times 10^{-4}~\rm s^{-1}$. Calculate the concentration of $\rm N_2O_5$ remaining after one hour when the initial concentration of $\rm N_2O_5$ was 0.40 mol L⁻¹. What percentage of $\rm N_2O_5$ has reacted?

5. Three experiments were performed for the following reaction:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

The following data were obtained:

Experiment	Inital conc	entration	Initial rate
	[Cl ₂]	[NO]	$(\text{mol } L^{-1} \text{ s}^{-1})$
I	0.02	0.01	2.40×10^{-4}
II	0.02	0.03	2.16×10^{-3}
III	0.04	0.03	4.32×10^{-3}

Determine (a) the orders with respect to Cl₂ and NO, (b) rate law, and (c) rate constant.

6. During the decomposition of N₂O₅ dissolved in carbon tetrachloride at 303 K, the following results were obtained:

Tr. ()						unicu.
Time (min)	0	40	80	120	160	90
Vol of O ₂	0	15.6	28.6	38.6		84.6
collected (mL)			20.0	36.0	40.8	84.6
					=	

Show that the reaction is of first order. Also calculate the rate constant.

7. Diazobenzene chloride decomposes as:

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

The volume of N₂ evolved at different times was measured and following results were obtained:

Time (min)	0	20	70	00
Vol of N ₂ (mL)	0	10	33	162

Calculate the (a) order of reaction and (b) rate constant.

- 8. An acidic solution of sugar was hydrolyzed to the extent of 57% after 66 min. Assuming the reaction to be of first order, calculate the time taken for 75% hydrolysis.
- 9. The rate constant for the decomposition of N_2O_5 is 6.0×10^{-4} s⁻¹. At what time will the initial concentration of 1 M be reduced to 0.2 M if the reaction is of first order?
- **10.** Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply.

A study at 35°C gave the following results:

Time (min)	0	15	30	45	60
Number of bacteria	50	100	200	400	800

Show that the rate of production of bacteria is of first order. How many bacteria will be there after 3 hours?

- 11. In milk at 37°C lactobacillus acidophilus has a generation time of about 75 min. Calcualte the populaion relative to the initial value at 30 min.
- 12. The rate of decomposition of hydrogen peroxide at a particulat temperature was measured by titrating its solution with acidic KMnO₄ solution. Following results were obtained:

Time, t (min)	0	10	20
mol (KMnO ₄)	22.8	13.8	8.3

- a. Show that the reaction is of first order.
- **b.** Calculate the rate constant.
- 13. The following data were obtained for the decomposition of NO in contact with gold surface at 900°C. Find the order of reaction.

Time (min)	15	30	45	65	80
% decomposition	17	32	44.5	57	65

14. Cane sugar is gradually converted into dextrose and laevulose by dilute acid. The rate of inversion is observed by measuring the polarization angle, at various times, when the following results are obtained:

Time (min)	0	10	20	30	40	100	8
Angle	32.4	28.8	25.5	22.4	19.6	-6.1	-14.1

Show that the reaction is of first order. Calculate the value of t, when the solution is optically inactive.

15. 1 mL of methyl acetate was added to a flask containing 20 mL of N/20 HCl maintained at 25°C. 2 mL of reaction

mixture was withdrawn at different intervals and titrated mixture and alkali solution. The following results were with a standard alkali solution.

obtained.	0	75	119	183	∞ .
Time (min)	19.24	24.20	26.60	29.32	42.03

Show that the reaction follows first order kinetis.

The rate of a certain reaction depends on the concentration according to the equation:

$$\frac{-d[c]}{dt} = \frac{k_1 c}{1 + k_2 c}$$

What will be the order of reaction, when concentration (c)

- b. Very low a. Very high
- 17. Areaction "A" proceeds in parallel channels $A \stackrel{\textstyle >}{\underset{}{\nwarrow}} B$. Although the branch A o B, product B may dominate in quantity over C. Why may this be so? Suppose the half life values for the two branches are 60 min and 90 min, what is the overall half life value?
- 18. Surface-catalyzed reactions that are inhibited by the products obey the rate equation (in same cases):

$$\frac{dx}{dt} = \frac{k(a-x)}{1+bx}$$
, where a is the initial concentration of the

reactant and k and b are constants. x is the concentration of products at any time t and the reaction is $A \rightarrow B$.

- a. Integrate the above equation.
- b. Derive an expression for $t_{1/2}$.
- 19. For a reversible first order reaction.

$$A \stackrel{k_1}{\longleftarrow} B; k_1 = 10^{-2} \text{ s}^{-1}$$

and
$$\frac{[B]_{eq}}{[A]_{eq}} = 4$$
. If $[A]_0 = 0.01$ M and $[B]_0 = 0$

What will be the concentration of B after 30 s?

- 20. Show that the time $\frac{t_{1/2}}{t_{3/4}}$, for *n*th order reaction is a function
 - of *n* alone. $t_{3/4}$ is the time required for concentration to become one-fourth of the original concentration.
- 21. The conversion of trypsinogen (A) into trypsin (B) is an autocatalytic reaction $A \rightarrow B$ where B catalyzes the

reaction. The rate equation is: $\frac{-dx}{dt} = kxy$, where x and y

are concentrations of trypsinogen at time t.

- a. Integrate this equation for initial concentration of x_0 and y_0 for A and B, respectively.
- **b.** Show that $kt = \frac{2.303}{(x_0 + y_0)} \log \frac{y \cdot x_0}{x \cdot y_0}$
- 22. The oxidation of certain metal is found to obey the equation: $A^2 = \alpha t + \beta$, where A is the thickness of the oxide film at time t; α and β are constants. What is the order of this reaction?

23. The inversion of cane sugar proceeds with constant $t_{1/2} = 500$ min, at pH = 5 for any concentratrion of sugar. However, if pH = 6, $t_{1/2}$ changes to 50 min. Derive the rate law for inversion of cane sugar.

ANSWERS

- 2. Ist order 3. 72.12 min 1. 157.8 min
- **4.** (a) $[N_2O_5]_{left} = 0.041 \text{ M}$ (b) % of N_2O_5 reacted = 89.75%
- **5.** (a) Order w.r.t. $Cl_2 = 2$, order w.r.t. NO = 1
 - (b) Rate = $k[NO][Cl_2]^2$ (c) $K = 1.2 \times 10^2 \text{ mol}^{-2} L^2 \text{ s}^{-1}$
- **6.** $k = 5.08 \times 10^{-3}$ **7.** (a) OR = 1, (b) $k = 3.21 \times 10^{-3} \text{ min}^{-1}$
- **10.** 2.04×10^5 **9.** 2683 s 8, 108.4 min
- **12.** (a) yes (b) $k = 0.5037 \text{ min}^{-1}$ 11. 1.32
- **14.** t = 86.5 min15. yes 13. Ist order
- 17.36 min 16. First order

18. (a)
$$k_l = (1 + ab)\log\left(\frac{a}{a - x}\right) - bx$$

(b)
$$t_{1/2} = \frac{\log 2 + ab(\log 2 - 0.5)}{k}$$

- **20.** The ratio depends only on n. **19.** 2.50×10^{-3} M
- **22.** First order **23.** r = k (sugar) 21. Factual

4.12 THEORIES OF CHEMICAL KINETICS

We have already noted that a complex reaction involves a number of elementary steps. The mechanism of a reaction includes the sequence of elementary steps by which the reactant molecules are converted into products. The necessary condition for any mechanism proposed is that the rate law expression derived on the basis of this mechanism should agree with the experimentally determined rate law. We do not have any general theory for rates of complex reactions. However, there have been several approaches to calculate the rate constant of elementary reactions. The elementary reactions may be unimolecular in which one molecule of the reactant is converted into the product(s). A bimolecular reaction may involve combinations of two molecules or exchange of atoms or group of atoms between the two reactant molecules. In a termolecular reaction, three reactant molecules take part in the reaction simultaneously. The temperature dependence of the rate constants for elementary reactions has helped a great deal in the development of various theories of reaction rates.

4.12.1 TEMPERATURE DEPENDENCE OF THE RATE OF A REACTION

Temperature has a great influence on the reaction rate. In general, an increase in temperature increases the rates of almost all reactions. On the other hard, a decrease in temperature decreases the rate.

For example, in the decomposition of N₂O₅, the time taken for half of the original amount of material to decompose is 12 min at 50°C, 5 hr at 25°C and 10 days at 0°C. Similarly, in a mixture of potassium permanganate (KMnO₄) and oxalic acid (H₂C₂O₄), potassium permanganate gets decolourized faster at a higher temperature than that at a lower temperature.

It has been found that for a chemical reaction with rise in temperature by 10°C, the rate constant is nearly doubled and is called temperature coefficient.

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation. It was first proposed by Dutch chemist, J.H. van't Hoff but Swedish chemist Arrhenius provided its physical justification and interpretation.

$$k = Ae^{-Ea/RT} \qquad ...(i)$$

where A is the Arrhenius factor or the frequency factor for binary collisions. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is the gas constant and E_a is the activation energy measured in joules per mole (J mol⁻¹). The two quantities A and E_a are collectively called Arrhenius parameters.

Equation (i) tells us that the rate constant increases exponentially with the increase of temperature.

It can be understood clearly by considering the following simple reaction:

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

The energy required to form this intermediate, called activated complex (C), is known as activation energy (E_a) . Fig. 4.12 is obtained by plotting potential energy vs reaction coordinate. Reaction coordinate represents the profile of energy changes when reactants change into products.

Some energy is released when the complex decomposes to form products. So, the final heat of the reaction depends upon the nature of reactants and products. From Fig. 4.12, it may be noted that

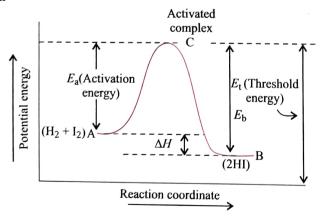


Fig. 4.12 Diagram showing the plot of potential energy vs reaction coordinate

Threshold energy = Activation energy + Energy possessed by

the reactants

All the molecules in the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of any one molecule with precision, Ludwig Boltzann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules. According to them, the distribution of kinetic

energy may be described by plotting the fraction of molecules (N_E/N_T) with a given kinetic energy E vs kinetic energy (Fig. 4.13). Here, N_E is the number of molecules with energy E and N_T is total number of molecules.

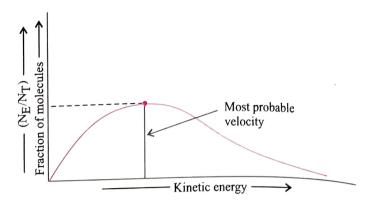


Fig. 4.13 Distribution curve showing energies among gaseous molecules

The peak of the curve corresponds to the most probable kinetic energy, i.e., the kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher or lower than this value. When the temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 4.14) and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of E_a on Maxwell Boltzmann distribution curve (Fig. 4.14). **Refer to Overview point 24 also.**

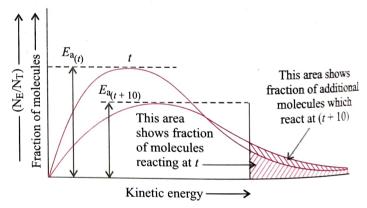


Fig. 4.14 Maxwell and Boltzmann distribution curve showing temperature dependence of rate of a reaction

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than $E_{\rm a}$. It is clear from the diagram that in the curve at (t+10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation (i) the factor $e^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a and is called *Boltzmann factor*. Taking natural logarithm of both sides of Eq. (i)

$$\ln k = -\frac{E_a}{RT} + \ln A \text{ or } \log k = \log A - \frac{E_a}{2.303RT}$$
 ...(ii)

It has been found that for a chemical reaction with rise in temperature by 10°C, the rate constant is nearly doubled and is called temperature coefficient.

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$$A$$
 is the Arrhenius factor or the frequency factor for binary collisions. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is the gas constant and E_a is the activation energy measured in joules per mole (J mol⁻¹). The two quantities A and E_a are collectively called Arrhenius parameters.

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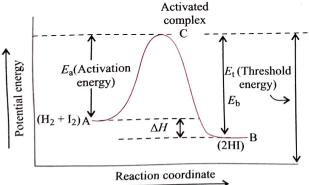


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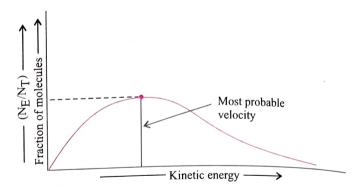


Fig. 4.13 Distribution curve showing energies among gaseous molecules

The peak of the curve corresponds to the most probable kinetic energy, i.e., the kinetic energy of maximum fraction of molecules. There are decreasing number of molecules with energies higher or lower than this value. When the temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 4.14) and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times. We can mark the position of $E_{\rm a}$ on Maxwell Boltzmann distribution curve (Fig. 4.14). **Refer to Overview point 24 also.**

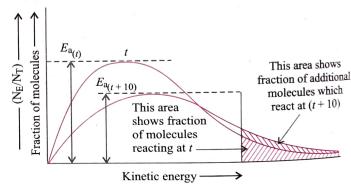


Fig. 4.14 Maxwell and Boltzmann distribution curve showing temperature dependence of rate of a reaction

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than $E_{\rm a}$. It is clear from the diagram that in the curve at (t+10), the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

In the Arrhenius equation (i) the factor $e^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a and is called *Boltzmann factor*. Taking natural logarithm of both sides of Eq. (i)

$$\ln k = -\frac{E_a}{RT} + \ln A \text{ or } \log k = \log A - \frac{E_a}{2.303RT}$$
 ...(ii)

The plot of $\ln k$ or $\log k$ vs 1/T gives a straight line according to Eq. (ii) as shown in Fig. 4.15.

Intercept = $\ln \Delta$ or Ω .

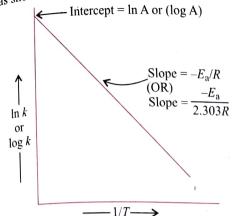


Fig. 4.15 A plot between $ln\ k$ or $log\ k$ and 1/T

Thus, it has been found from Arrhenius equation (i) that increasing the temperature or decreasing the activation energy will result in an increase in the rate of reaction and an exponential increase in the rate constant.

4.12.2 CALCULATION OF ACTIVATION ENERGY AND FREQUENCY FACTOR (A)

The activation energy can be calculated from Eq. (ii). As is clear the equation is in the form y = mx + c which represents a straight line. When $\log k$ is plotted against 1/T, we get a straight line. The intercept of this line which is equal to $\log A$ and the slope is equal to $-\frac{E_a}{2000R}$.

$$\therefore \text{ Slope} = -\frac{E_a}{2.303R} \qquad \dots \text{(iii)}$$

Knowing the value of slope and gas constant R, the activation energy can be calculated as

$$E_a = -2.303R \times \text{Slope}$$

Alternatively, $E_{\rm a}$ and A can be determined by measuring the values of rate constant at two different temperatures. Let k_1 and k_2 are the rate constants for the reaction at two different temperatures T_1 and T_2 , respectively. Then,

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1} \qquad ...(iv)$$

and
$$\log k_2 = \log A - \frac{E_a}{2.303RT_2}$$
 ...(v)

Subtracting Eq. (v) from (iv), we get

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

or
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

= $\frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$...(vi)

4.12.3 COLLISION THEORY

We have learnt that the basic requirement for a reaction to occur is that the reacting species (atoms, molecules, or ions) must collide with one another. This is also the basis of *collision theory* for reactions. It is based on the kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur when molecules collide with each other. The number of collisions that takes place per second per unit volume of the reaction mixture is known as *collision frequency* Z. The value of collision frequency is normally very high. For instance, under ordinary conditions of temperature and pressure, in a gaseous system, the collision frequency of binary collisions is of the order of 10^{25} to 10^{28} . If all the collisions are effective in forming the products, the reactions must be completed in a very short time. However, in actual practice, most of the chemical reactions are slow and take much longer time for their completion.

This means that all the collisions among the reacting species at a given temperature are not effective in bringing about the chemical reaction. The collisions which actually produce products and, therefore, result in chemical reactions are called *effective collisions*.

There are two important barriers to a reaction, namely (a) energy barrier and (b) orientation barrier.

a. Energy factor: For a collision to be effective the colliding molecules must have energy more than a particular value. The minimum energy which the colliding molecules must have in order that the collision between them may be effective is called *threshold energy*. Thus, at ordinary temperature, and pressure, most of the molecules may not possess energy equal to or greater than the threshold value. In the graph (Fig. 4.16), E corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

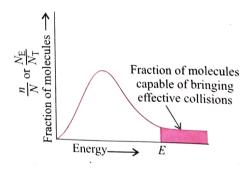


Fig. 4.16

The minimum amount of energy required by reactant molecules to participate in a reaction is called *activation* energy.

Activation energy = Threshold energy – Average kinetic energy of reacting molecules

Threshold energy = Initial potential energy of reactant molecules + Activation energy

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the activated complex. The life span of an activated complex is very small. Thus, an activated complex breaks either into reactants again or new substances, i.e., products. The activation energy $(E_{\rm a})$ depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions versus the progress of the reaction are shown in Fig. 4.17.

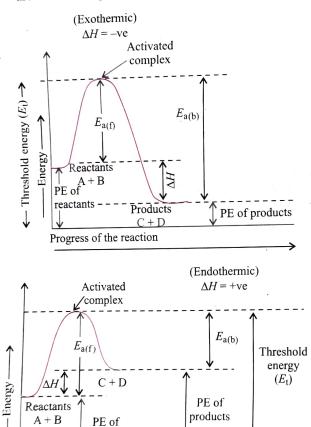


Fig. 4.17 Activation energy of exothermic and endothermic reactions

reactants

Progress of the reaction

Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, i.e., the number of effective collisions will increase and the rate of reaction will also increase.

Activation energy, $E_a = E_{\text{(activated complex)}} - E_{\text{(ground state)}}$ $\Delta H = \text{Activation energy of forward reaction } [E_{a(f)}] -$ Activation energy of backward reaction $[E_{a(b)}]$

b. Orientation factor: In some cases it is found that even if a large number of colliding molecules have energy more than the threshold value, still the reaction is slow. This is because of improper orientation of the colliding molecules at the time of collision, as shown in Fig. 4.18.

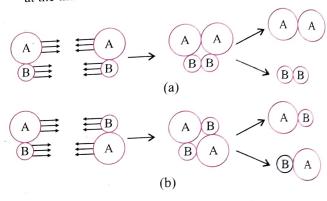


Fig. 4.18 Illustration of orientation factor for (a) effective collision and (b) ineffective collision

Another example of proper and improper orientation is the formation of CH3OH from CH3Br with OH ions, which depends upon the orientation of reactant molecules as shown in Fig. 4.19.

The proper orientation of reactant molecules leads to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

$$CH_{3}Br + OH \longrightarrow CH_{3}OH + Br^{\odot}$$

$$Improper \\ H \longrightarrow C \longrightarrow Br + OH$$

$$Improper \\ H \longrightarrow C \longrightarrow Br \longrightarrow OH$$

$$OH \longrightarrow C \longrightarrow Br$$

$$Intermediate$$

$$H \longrightarrow H$$

$$OH \longrightarrow C \longrightarrow H$$

$$OH \longrightarrow C \longrightarrow H$$

$$H$$

$$OH \longrightarrow C \longrightarrow H$$

$$H$$

Fig. 4.19 Diagram showing molecules having proper and improper orientation

Thus, the collisions in which the colliding molecules do not possess the minimum energy for effective collisions (threshold energy) or proper orientation, do not form products.

Relationship Between Rate of Reaction and Collision

Median elementary molecular reaction

 $_{A+B} \longrightarrow Products,$

is the collision frequency and f is the fraction of molecules all solutions are effective, then evidently ilZAB is collisions are effective, then evidently

Rate of reaction =
$$\frac{-dx}{dt} = Z_{AB} \times f$$
 ...(i)

Now, as the rate of a chemical reaction depends upon the activation

 $f = e^{-Ea/RT}$ (fraction of molecules with energies equal to or greater than E_a) (called Boltzmann factor)

Thus, equation (i) becomes

Rate =
$$Z_{AB} e^{-Ea/RT}$$

To account for effective collisions, another factor P, called the and all and account the fact of the fact o that in a collision, molecules must be properly oriented, i.e.,

Rate =
$$(PZ_{AB})e^{-Ea/RT}$$
 (or $PZ_{AB} = A$)

 $_{\rm i.c.,\,Arrhenius}$ factor A is equal to the collision frequency $(Z_{\rm AB})$ multiplied by probability or steric factor (P). Thus, in collision theory, E_a and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

The main points of collision theory are summed up below:

- a. For a reaction to occur, there must be collisions between the reacting species.
- b. Only a certain fraction of the total number of collisions are effective in forming the products.
- c. For effective collisions, the molecules should possess sufficient energy as well as orientation.

Limitation of Collision Theory

Collision theory has certain limitations as it considers atoms/ molecules to be hard spheres and ignores their structural aspect.

4.12.4 EFFECT OF CATALYST

Acatalyst is a substance that can alter the rate of a reaction without itself undergoing any permanent chemical change.

The action of a catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. 4.20.

It is clear from Arrhenius equation $(k = Ae^{-Ea/RT})$ that lower the value of activation energy faster will be the rate of a reaction.

A small amount of the catalyst can catalyze a large amount of reactants. A catalyst does not alter Gibbs energy (ΔG) of a reaction. It catalyzes the spontaneous reactions but does not catalyze non-spontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction, rather it helps in attaining the equilibrium faster, that is, it catalyzes the

forward as well as backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

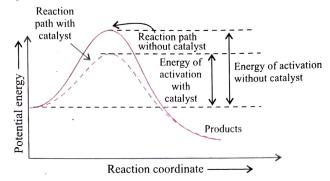


Fig. 4.20 Effect of catalyst on activation energy

Classification of Catalysts

Catalyst can be classified into two categories: (a) positive catalyst and (b) negative catalyst.

a. Presence of positive catalyst

The function of a positive catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. In the presence of a catalyst, the reaction follows a path of lower activation energy. Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. Fig. 4.21 shows how the activation energy is lowered in the presence of a catalyst.

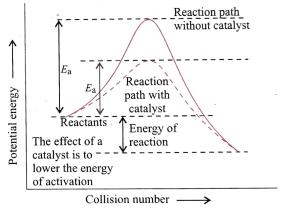


Fig. 4.21 Lowering of activation energy by a positive catalyst

b. Presence of negative catalyst

A negative catalyst increases the activation energy of reaction by forming a new intermediate of high energy, i.e., by changing the reaction mechanism.

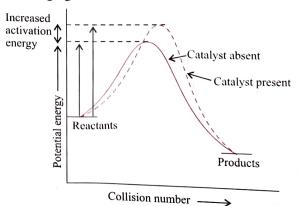


Fig. 4.22 Increase in the activation energy by a negative catalyst

Due to increased activation energy, some active molecules become inactive, therefore, the rate of reaction decreases. (Fig. 4.22)

Activation Energy Diagram for a Two-Step Reaction

Suppose a reaction $A \rightarrow C$ takes place in two steps:

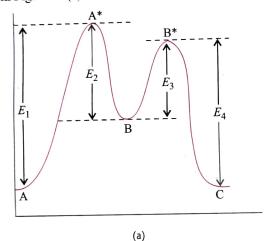
$$A \xrightarrow{Step(i)} B \xrightarrow{Step(ii)} C$$

To know whether step (i) or step (ii) is the slow step (i.e., rate-determining step)., study of $E_{\rm a}$ separately for each step is required. These two steps are written as:

Step (i) A
$$\xrightarrow{E_1}$$
 A* $\xrightarrow{-E_2}$ B

Step (ii) B
$$\xrightarrow{E_3}$$
 B* $\xrightarrow{-E_4}$ C

If $A \rightarrow C$ is an exothermic reaction, the two possibilities are shown in Figs. 4.23(a) and 4.23(b).



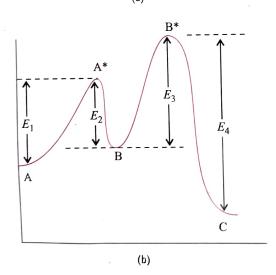


Fig 4.23

In Fig. 4.23(a), $E_1 > E_3$, therefore, step (i) is slow and rate-determining step.

In 4.23(b), $E_1 < E_3$, therefore, step (ii) is slow and rate-determining step.

4.12.5 THERMODYNAMIC AND KINETIC STABILITY

A reaction is feasible only if ΔG is negative. Such a reaction is called thermodynamically unstable. For example, the reaction

between hydrogen arid oxygen is thermodynamically unstable since change in free energy for the reaction is negative.

$$H_2(g) + 1/2O_2(g) \longrightarrow H_2O(1)$$

However, a mixture of hydrogen and oxygen do not combine spontaneously to form water. The reason for this is that initially the molecules of reactant (H_2 and O_2) require the absorption of a definite amount of energy (E_a) in order to reach the activated state, from which they give products and liberate the heat of reaction. Thus, we say that a mixture of H_2 and O_2 is kinetically stable at room temperature. From the above discussion, it is clear that every reaction, feasible from the point of view of free energy change, need not necessarily take place; and many such reactions may be prevented from occurring by high activation energy barrier. Such reactions though thermodynamically unstable (or energetically feasible) are kinetically stable at ordinary temperature.

4.12.6 ACTIVATED COMPLEX

During a chemical reaction certain bonds are broken and certain new bonds are formed. The breaking of bonds requires energy, whereas the formation of bonds results in the release of energy. For example, in the reaction between H₂ and I₂ to form HI, when H₂ molecule approaches I₂ molecules, H—H and I—I bonds start breaking and HI bonds start forming. In the beginning breaking of bonds predominates, so the energy of the system starts increasing and reaches a maximum called threshold energy. Then the energy starts decreasing because after this, the bond formation predominates and finally leads to the product hydrogen iodide. The arrangement of atoms corresponding to energy maxima (threshold energy) is called *activated complex*. In this state, the system has partial reactant character and partial product character.

Distinction Between Unstable Intermediate and Transition State or Activated Complex

An unstable intermediate is an actual chemical species (which perhaps can be stabilized under different reaction conditions). It has normal bond orders for its atoms. It represents a minimum on the PE curve, albeit a small minimum (Fig. 4.24).

The activated complex or transition state (TS) is the postulated species which has maximum energy during the conversion from reactants to products. No matter which way the bond lengths and strength vary, stabilization results. The bond order of the atoms of the activated complex are sometimes unusual.

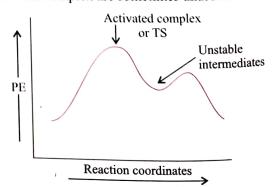


Fig. 4.24 Representation of activated complex (TS) and unstable intermediate in a chemical reaction

4.12.7 EXPOSURE OF RADIATIONS certain reactions are called photochemical reactions are called photochemical reactions. Certain reactions are called photochemical reactions.

Such reactions are called photochemical reactions.

The rate of a photochemical reaction is affected by the The late the period is affected by the more than the period is a photochemical reaction may not be a period in the period in the period in the period is a period in the period in the period in the period is a period in the period in t m^{chsity} or m_s . The energy absorbed by the reaction as m_s and m_s and m_s and m_s and m_s and m_s are energy absorbed by the reaction m_s and m_s are energy absorbed by the reaction m_s and m_s are energy absorbed by the reaction m_s and m_s are energy absorbed by the reaction m_s and m_s are energy absorbed by the reaction m_s and m_s are energy m_s are energy m_s and m_s are change (AU) of the light energy absorbed by the reactants changes into a part of the highest products. For example, ΔG is positive for the fire energy by the products.

$$\underset{H_2}{\text{tion}} \longrightarrow 2\text{HCl}$$

4.12.8 PHOTOSENSITIZER

his a substance which when added to a reaction mixture helps It is a social the photochemical reaction without undergoing chemical change itself. This phenomenon is known as to known as thomsensitization, e.g., chlorophyll acts as photosensitizer in the photosynthesis.

4.12.9 VISION

Vision involves geometrical isomerization of a compound retinal m unsaturated aldehyde) present in the eye by absorbing the light illing on it, a photochemical reaction.

4.12.10 QUANTUM YIELD OR QUANTUM EFFICIENCY OF A PHOTOCHEMICAL REACTION

Different photochemical reactions have different values of quantum efficiency depending upon their mechanisms. For example photosynthesis of HBr has low value of ϕ while photosynthesis of HCl has very high value of ϕ .

2. Autocatalysis is a phenomenon in which the product formed is itself a catalyst and thereof enhances the rate.

- b. Promoters are substances which do not act as catalyst but enhance the efficiency of a catalyst.
- c. Negative catalyst or inhibitors are those substance which decrease the rate of a reaction.
- d. Catalyst can be poisoned by many substances.

ILLUSTRATION 4.124

The rate constants of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} , respectively. Calculate the values of E_a and A

Sol.
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{0.07}{0.02} = \left(\frac{E_{\rm a}}{2.303 \times 8.314 \,\mathrm{J \, K^{-1} \, mol^{-1}}}\right) \left[\frac{700 - 500}{700 \times 500}\right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4}/19.15$$

$$E_{\rm a} = \frac{0.544 \times 19.15}{5.714 \times 10^{-4}} = 18230.8 \,\text{J}$$

Since
$$k = Ae^{-E_{a}/RT}$$

$$\log k = \log A - \frac{E_{\rm a}}{2.303RT}$$

$$\log A = \log k + \frac{E_{\rm a}}{2.303RT}$$

$$\log A = \log(0.02) + \frac{18230.8 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}$$
$$= -1.699 + 1.90 = 0.201 \approx 0.2$$
$$A = \text{Antilog}(0.2) \approx 1.585 \approx 1.6$$

ILLUSTRATION 4.125

The first order rate constant for the decomposition of C₂H₅I by the reaction.

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

at 600 K is 1.60×10^{-5} s⁻¹. Its energy of activation is 209 kJ mol-1. Calculate the rate constant at 700 K.

Sol. We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$= \log (1.60 \times 10^{-5}) + \frac{209 \times 10^{3} \text{ J mol}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{K}^{-1}}$$

$$\times \left[\frac{100}{600 \times 700} \right] K$$

$$\log k_2 = -4.796 + 2.599 = -2.197$$

$$k_2 = \text{Antilog}(-2.197)$$

$$=$$
 Antilog $(-2.197 + 1 - 1)$

= Antilog
$$(\overline{3}.803) = 6.36 \times 10^{-3} \text{ s}^{-1}$$

ILLUSTRATION 4.126

The number of flashes of a firely change with temperature is as follows:

T° (C)	Number of flashes/min	T° (C)	Number of flashes/min
25	7	38	47
- 28	10	42	82
32	20	44	108
35	31		

Determine the energy of activation for the chemical reaction that leads to the flash. $(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$

Sol.
$$k_1 = 7 \text{ min}^{-1}$$
, when $T_1 = 298 \text{ K}$
 $k_2 = 10 \text{ min}^{-1}$, when $T_2 = 301 \text{ K}$
 $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$
 $\log \frac{10}{7} = \frac{E_a}{2.303 \times 8.314} \times \left[\frac{301 - 298}{301 \times 298} \right]$
 $\therefore E_a = 88.678 \text{ kJ mol}^{-1}$

ILLUSTRATION 4.127

If a catalyst drops the activation energy of a reaction at 25°C from 80 kJ to 40 kJ, what is the magnitude of the affect on the forward reaction rate and reverse rate?

Sol.
$$E_a = 80 - 40 = 40 \text{ kJ}$$

a. $k_1 = Ae^{-E_a/RT}$
 $k_2 = Ae^{-E_a(c)/RT}$
 $\log \frac{k_2}{k_1} = \frac{E_a - E_a(c)}{2.3 \times 8.314 \times 298 \text{ K}}$
 $= \frac{40 \times 10^3 \text{ J}}{2.3 \times 8.314 \times 298 \text{ K}} = 7.0$
 $\therefore \frac{k_2}{k_1} = 10^7$

The reaction rate increases by 10^7 times.

b. Since catalyst increases the rate of reaction but does not affect the equilibrium of the reaction. Therefore, $r_f = r_b$.

ILLUSTRATION 4.128

What is the value of the rate constant, predicated by the Arrhenius's equation if $T \to \infty$? Is this value physically reasonable?

Sol. If
$$T \to \infty$$
, $k = A e^{-E_a/RT} = Ae^0 = A$

i.e., rate constant = collision frequency which is not feasible.

Alternatively

If
$$k = A$$
 $e^{-E_a/RT} = 1$
 $\therefore \frac{E_a}{RT} = 0$, $E_a = 0$

Since the activation energy cannot be zero, the result is not physically reasonable.

ILLUSTRATION 4.129

The pre-exponential factor for the free radical addition of chlorine is 2×10^{13} s⁻¹. Find the rate constant of this reaction at STP.

$$E_a = 0.$$

 $k = Ae^{-E_a/RT}$ (if $E_a = 0$)
 $k = A = 2 \times 10^{13} \text{ s}^{-1}$.

ILLUSTRATION 4,130

The rate constant of a certain reaction is given by:

$$\log k = 5.4 - \frac{212}{T} + 2.17 \log T$$

Calculate E_a at 127°C.

Sol.
$$\log k = 5.4 - \frac{212}{T} + 2.17 \log T$$
 ...(i)

Multiply Eq. (i) by 2.3,

$$2.3 \log k = 5.4 \times 2.3 - \frac{212 \times 2.3}{T} + 2.17 \times 2.3 \log T$$

$$\ln k = 5.4 \times 2.3 - \frac{212 \times 2.3}{T} + 2.17 \ln T$$

$$\frac{d}{dt}(\ln k) = 0 + \frac{212 \times 2.3}{T^2} + \frac{2.17}{T} = \frac{487.6 + 2.17T}{T^2} \dots (ii)$$

$$\frac{d}{dt}(\ln k) = E_a / RT^2 \qquad \dots (iii)$$

Compare Eqs. (ii) and (iii).

$$\frac{E_{\rm a}}{RT^2} = \frac{487.6 + 2.17T}{T^2}$$

$$\frac{E_{\rm a}}{R}$$
 = 487.6 + 2.17 T (R = 1.98 \approx 2 cal)

$$E_a = 2 \text{ cal}[487.6 + 2.17 \times 400] = 2711.2 \text{ cal}$$

ILLUSTRATION 4.131

Two first order reactions proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C.

Sol. For first order,
$$r_1 = k$$
 [A]

$$\frac{r_1}{r_2} = \frac{k_1}{k_2}$$
 = temperature coefficient

Let the rate of the reaction for first reaction at 25°C be r_1 and rate of reaction for second reaction at 25°C be r_2 .

$$r_1 = r_2$$

	Rates of reac	tion
At 25°C	r_1	r,
35°C	$2r_1$	$3r_2$
45°C	$(2)^2r_1$	$(3)^2 r_2$
55°C	$(2)^3r_1$	$(3)^3 r_2$
65°C	$(2)^4r_1$	$(3)^4 r_2$
75°C	$(2)^5 r_1$	$(3)^5 r_2$

Temperature coefficient for first reaction = $\frac{k_{35}}{k_{25}} = \frac{r_{35}}{r_{25}} = 2$ i.e., for each 10°C rise in temperature, rate becomes 2 times

Similarly, for second reaction, it becomes 3 times.

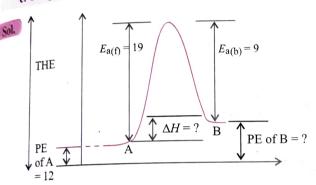
$$=\frac{(3)^5 r_2}{(2)^5 r_1} = 7.5937$$

$$(: r_1 = r_2)$$

ILLUSTRATION 4.132

For a reaction $A \to B$, E_a for the forward reaction $E_{a(f)}$ and For a reaction $E_{a(b)}$ is 19 kJ mol⁻¹ and 9 kJ mol⁻¹, hackward. Potential energy of A is 12 kJ mol⁻¹. Calculate

- a. The threshold energy of reaction (THE)
- b. The heat of the reaction
- c. The potential energy of products (PE)



a. THE =
$$19 + 12 = 31 \text{ kJ mol}^{-1}$$

b.
$$\Delta H = 19 - 9 = 10 \text{ kJ mol}^{-1}$$

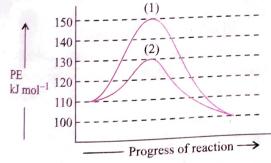
c. PE of product = THE
$$-E_a(b)$$

= 31 $-9 = 22 \text{ kJ mol}^{-1}$

LLUSTRATION 4.133

Given the following graph.

a. Calculate ΔH for the reaction and energy of activation for the forward and backward reaction.



- b. Curve (2) is the energy profile in the presence of a catalyst. What is the energy of activation for the two reactions in the presence of a catalyst?
- c. Will the catalyst change the extent of the reaction?

a. $\Delta H = 100 - 110 = -10 \text{ kJ mol}^{-1}$

$$E_{\rm a(f)} = 150 - 110 = 40 \text{ kJ mol}^{-1}$$

$$E_{\rm a(b)} = 150 - 100 = 50 \text{ kJ mol}^{-1}$$

b. $E_{a(f)}$ with catalyst = 130 - 110 = 20 kJ $E_{a(b)}$ with catalyst = 130 - 100 = 30 kJ c. Catalyst does not change the extent of the reaction it only increases the rate of reaction.

ILLUSTRATION 4.134

At 407 K, the rate constant of a chemical reaction is 9.5×10^{-5} $\rm s^{-1}$ and at 420 K, the rate constant is 1.9 \times 10 $^{-4}$ $\rm s^{-1}.$ Calculate the Arrhenius parameter of the reaction.

Sol. The Arrhenius equation is,

$$\log \frac{k_2}{k_1} = \frac{E_{\text{a}}}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given:
$$k_1 = 9.5 \times 10^{-5} \text{ s}^{-1}$$
; $k_2 = 1.9 \times 10^{-4} \text{ s}^{-1}$;

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1};$$

$$T_1 = 407 \text{ K} \text{ and } T_2 = 420 \text{ K}$$

Substituting the values in Arrhenius equation

$$\log \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} = \frac{E_{\text{a}}}{2.303 \times 8.314} \left[\frac{420 - 407}{420 \times 407} \right]$$

$$E_{\rm a} = 75782.3~{\rm J~mol^{-1}}$$

Applying now log
$$k_1 = \log A - \frac{E_a}{2.303RT_1}$$

$$\log 9.5 \times 10^{-5} = \log A - \frac{75782.3}{2.303 \times 8.314 \times 407}$$

or
$$\log \frac{A}{9.5 \times 10^{-5}} = \frac{75782.3}{2.303 \times 8.314 \times 407} = 9.7246$$

$$A = 5.04 \times 10^5 \text{ s}^{-1}$$

Note: k and A are expressed in the same units.

ILLUSTRATION 4.135

The rate of a reaction triples when temperature changes from 20°C to 50°C. Calculate the energy of activation for the reaction $(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}).$

Sol. The Arrhenius equation is

$$\log \frac{k_2}{k_1} = \frac{E_a}{R \times 2.303} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given:
$$\frac{k_2}{k_1} = 3$$
; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$;

$$T_1 = 20 + 273 = 293 \text{ K}; T_2 = 50 + 273 = 323 \text{ K}$$

Substituting the given values in the Arrhenius equation,

$$\log 3 = \frac{E_{\rm a}}{8.314 \times 2.303} \left[\frac{323 - 293}{323 \times 293} \right]$$

$$E_{\rm a} = \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30}$$

- $= 28811.8 \text{ J mol}^{-1}$
- $= 28.8118 \text{ kJ mol}^{-1}$

ILLUSTRATION 4.136

The energy of activation of a first order reaction is 187.06 kJ mol⁻¹ at 750 K and the value of pre-exponential factor A is $1.97 \times 10^{12} \text{ s}^{-1}$. Calculate the rate constant and half life. $(e^{-30} = 9.35 \times 10^{-14})$

Sol. Given
$$E_a = 187.06 \text{ kJ mol}^{-1}$$

$$T = 750 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

We know $k = Ae^{-E_a/RT}$

$$\therefore \frac{E_{\rm a}}{RT} = \frac{187.06 \times 10^3}{8.314 \times 750} \approx 30$$

$$k = Ae^{-30} = 1.97 \times 10^{12} \times 9.35 \times 10^{-14}$$
$$k = 0.184 \text{ s}^{-1}$$

Half life
$$(t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{0.184} = 3.76 \text{ s}$$

ILLUSTRATION 4.137

A reaction takes place in three steps: the rate constant are k_1 , k_2 , and k_3 . The overall rate constant $k = k_1 k_3 / k_2$. If the energies of activation are 40, 30, and 20 kJ mol⁻¹, the overall energy of activation is (assuming A to be constant for all)

Sol. c. The overall rate constant
$$k = \frac{k_1 k_3}{k_2}$$

We know; $k = Ae^{-E_a/RT}$

$$\therefore k = \frac{k_1 k_3}{k_2} = A e^{-(E_{a_1} + E_{a_3} - E_{a_2})/RT}$$

$$= Ae^{-(40-30+20)/RT}$$
$$= Ae^{-30/RT}$$

$$\therefore E_a = 30 \text{ kJ mol}^{-1}$$

ILLUSTRATION 4.138

Can a reaction have negative activation energy?

Sol. If E_a were negative, the exponential factor can be written as e^x where $x = E_a/RT$. If x < < 1, we have

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

= 1 + x (neglecting higher power of x)

$$=1+E_{a}/RT$$

 $\therefore k = A(1 + E_a/RT)$, i.e. k >> A which is impossible. Hence, E_a cannot be negative.

ILLUSTRATION 4.139

In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why?

Sol. This is because of improper orientation of the colliding molecules at the time of collision.

ILLUSTRATION 4.140

Why are reactions of higher order less in number?

Sol. A reaction takes place because molecules collide. The chances for a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher order are less.

ILLUSTRATION 4.141

In chemical kinetics, only a small fraction of collisions lead t_0 reactions. This is because

- a. The colliding molecules may not be appropriately oriented to one another and the collisions are not energetic.
- **b.** The colliding molecules are properly oriented to one another and the collisions are highly energetic.
- c. The colliding molecules are properly oriented to one another and the collisions are not highly energetic.
- d. The colliding molecules may not be appropriately oriented to one another and the collisions are very energetic.

Sol.

a. For effective collision molecules must have sufficient energy and proper orientation.

ILLUSTRATION 4.142

Can activation energy for reactions be zero?

Sol. In the Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

if E_a is zero, then k = A.

That is, every collision between molecules leads to the chemical reaction. This is not true. Thus, E_a cannot be zero.

ILLUSTRATION 4.143

The reaction

$$2NO_2 \rightarrow 2NO + O_2$$

has an activation energy of 110 kJ mol⁻¹. At 400°C, the rate constant is 7.8 mol⁻¹ L s⁻¹. What is the value of rate constant at 430°C?

Sol. We know that

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

 $E_{\rm a} = 110 \text{ kJ mol}^{-1}$

$$= 110 \times 10^{3} \text{ J mol}^{-1}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$k_1 = 7.8 \text{ mol}^{-1} \text{ L s}^{-1}$$

$$T_1 = 400 + 273 = 673 \,\mathrm{K}$$

$$k_2 = ?$$

$$T_2 = 430 + 273 = 703 \text{ K}$$

Substituting the values,

$$\log \frac{k_2}{7.8} = \frac{110 \times 10^3}{2.303 \times 8.314} \left[\frac{1}{673} - \frac{1}{703} \right]$$

$$= \frac{110 \times 10^3 \times (703 - 673)}{2.304 \times 8.314 \times 673 \times 703}$$

$$= 0.3643 \text{ or } \frac{k_2}{7.8} = 2.31$$

$$= 0.3043 \text{ ff } 7.8$$

$$0 \text{ ff } k_2 = 2.31 \times 7.8 = 18.0 \text{ mol}^{-1} \text{ L s}^{-1}$$

ILLUSTRATION 4.144 The activation energy of a first order reaction at 300 K is The activation at 300 K is $0 \text{ kJ} \text{ mol}^{-1}$. In the presence of a catalyst, the activation energy at 50 kJ mol} at 300 K. However, 60 kJ mol at 300 K. How many times the gets lowered than rate changes in the presence of a catalyst at the same temperature?

$$k_{1} = Ae^{-E_{a}/RT}$$

$$k_{2} = Ae^{-E_{a}(c)/RT}$$

$$\log \frac{k_{2}}{k_{1}} = \frac{E_{a} - E_{a(c)}}{2.303 RT}$$

$$\log \frac{k_{2}}{k_{1}} = \frac{6000 - 5000}{2.303 \times 8.314 \times 300} = 1.741$$

$$\frac{k_{2}}{k_{1}} = 55.08$$

The reaction rate increases by 55.08 times.

ILLUSTRATION 4.145

Given that the temperature coefficient for the saponification of ethylacetate by NaOH is 1.75. Calculate the activation energy.

$$\frac{k_2}{k_1} = 1.75$$
, $T_1 = 298 \text{ K}$ $T_2 = 308 \text{ K}$

(Since temperature coefficient is the ratio of rate constants at 35°C and 25°C)

$$2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$2.303 \log 1.75 = \frac{E_a}{1.987} \times \frac{308 - 298}{308 \times 298}$$

$$E_{\rm a} = \frac{2.303 \times 308 \times 298 \times 1.987}{10} \log 1.75 \text{ cal mol}^{-1}$$

= 10.207 kcal mol⁻¹

ILLUSTRATION 4.146

The energy of activation for a reaction is 100 kJ mol⁻¹. The presence of a catalyst lowers the energy of activation by 75%. What will be the effect on the rate of reaction at 20°C, other things being equal?

$$k = Ae^{-E_a/RT}$$

Case I:
$$k_1 = Ae^{-100/RT}$$
, $k_2 = Ae^{-25/RT}$

$$\frac{k_1}{k_2} = \frac{e^{-100/RT}}{e^{-25/RT}} = e^{-75/RT}$$

$$\log \frac{k_2}{k_1} = 75 / RT = \frac{75 \times 10^3}{8.314 \times 293} = 30.788$$

$$\frac{k_2}{k_1} = 2.35 \times 10^{30}$$

Case II: $r = k [A]^n$

 \therefore n and [A] are same for cases I and II.

$$\therefore \frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.35 \times 10^{30}$$

ILLUSTRATION 4.147

In the Arrhenius equation for a certain reaction, the values of A and E_a (energy of activation) are 4×10^{13} s⁻¹ and 98.6 kJ mol⁻¹, respectively. If the reaction is of first order, at what temperature will its life period be 10 min.

Sol.
$$k = Ae^{-E_a/RT}$$

= $4 \times 10^{13} e^{-(98.6 \times 10^3)/8.344 \times T}$

For first order,
$$k = \frac{0.693}{600} \,\text{s}^{-1}$$

$$\frac{0.693}{600} = 4 \times 10^{13} e^{-(98.6 \times 10^3)/8.314 \times T}$$

$$\log \frac{0.693}{600} = \log^4 \times 10^{13} - \frac{98.6 \times 10^3}{8.314 \times 2.303 \times T}$$

T = 311.35 K

ILLUSTRATION 4.148

How can the activation energy for a reaction be determined graphically?

- **a.** Plot k versus T, the slope of the line will be equal to E_{a} .
- **b.** Plot 1/[A], versus t, the slope of the line will be equal to
- **c.** Plot $\ln [A]_t$ versus t, the slope of the line be equal to
- **d.** Plot $\ln k$ versus 1/T, the slope of the line will be equal to $-E_a/R$.

Sol.

d.
$$k = Ae^{-E_a/RT}$$

or $\ln k = \ln A - \frac{E_a}{RT}$
Plot of $\ln k$ vs $\frac{1}{T}$
 $\ln A$
Slope = $\frac{-E_a}{R}$

ILLUSTRATION 4.149

The rate constant, activation energy, and Arrhenius parameter of a chemical reaction are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$, and $6.0 \times 10^{14} \, \mathrm{s}^{-1}$, respectively. The value of rate constant as $T \to \infty$ is

- **a.** $2.0 \times 10^{18} \text{ s}^{-1}$
- **b.** $6.0 \times 10^{14} \text{ s}^{-1}$
- c. 3.6×10^{30} s⁻¹
- d. None of these

Sol.

b. Given
$$k = 3.0 \times 10^{-4} \text{ s}^{-1}$$
; $A = 6.0 \times 10^{14} \text{ s}^{-1}$
 $E_a = 104.4 \text{ kJ mol}^{-1}$

Arrhenius equation is

$$k = Ae^{-E_{a}/RT}$$

as
$$T \to \infty$$

$$k = Ae^{-E_R/R \times \infty}$$
 or Ae^0

$$\left[\because \frac{-E_{a}}{R \times \infty} = 0 \right]$$

or
$$k = A$$

:.
$$k = 6.0 \times 10^{14} \text{ s}^{-1} \text{ as } T \to \infty$$
.

ILLUSTRATION 4.150

The rate constants k_1 and k_2 of two reactions are in the ratio 2: 1. The corresponding energies of activation of the two reactions will be related by

$$\mathbf{a}, E_1 > E_2$$

b.
$$E_1 \leq E_2$$

c.
$$E_1 = E_2$$

a.
$$E_1 > E_2$$
 b. $E_1 < E_2$ **c.** $E_1 = E_2$ **d.** $E_1 = 2E_2$

Sol.

b.
$$k_1/k_2 = 2 : 1$$
 or $k_1 = 2k_1$, i.e., $k_1 > k_2$. Using Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

Therefore, if k is high E_a is low. Hence, $E_2 > E_1$.

ILLUSTRATION 4.151

On introducing a catalyst at 500 K, the rate of a first order reaction increases by 1.718 times. The activation energy in the presence of a catalyst is 4.15 kJ mol⁻¹. The slope of the plot of $\ln k \, (s^{-1})$ against 1/T in the absence of catalyst is

$$\mathbf{d.} - 1000$$

Sol. d.

 $\frac{\text{Rate in the presence of catalyst}}{\text{Rate in the absence of catalyst}} = \text{Antilog} \left[\frac{+\Delta E}{2.303RT} \right]$

1.718 = Antilog =
$$\frac{E_{\rm a} - E_{\rm p}}{2.303 \times 8.314 \times 500}$$

Where $E_{\rm a}$ and $E_{\rm p}$ are energy of activation in absence and presence of catalyst.

$$E_{\rm a} - E_{\rm p} = 8.3 \times 500 \times 10^{-3}$$

$$E_{\rm a} = E_{\rm p} + (8.3 \times 500 \times 10^{-3}) = 4.15 + (8.3 \times 500 \times 10^{-3})$$

= 8.3 kJ mol⁻¹

$$\ln k = \ln A = \frac{E_{\rm a}}{R} \times \frac{1}{T}$$

Slope =
$$\frac{-E_a}{R} = \frac{-8.3 \times 1000}{8.3} = -1000$$

ILLUSTRATION 4,152

For which of the following reactions k_{310}/k_{300} would be maximum?

a. A + B
$$\rightarrow$$
 C; $E_a = 50 \text{ kJ}$ **b.** X + Y \rightarrow Z; $E_a = 40 \text{ kJ}$

b.
$$X + Y \rightarrow Z$$
; $E_a = 40 \text{ k}$.

c.
$$P + Q \rightarrow R$$
; $E_a = 60 \text{ k}$

c.
$$P + Q \rightarrow R$$
; $E_a = 60 \text{ kJ}$ d. $E + F \rightarrow G$; $E_a = 100 \text{ kJ}$

Sol.

d. Increase in the rate constant is maximum for the reaction having maximum activation energy.

ILLUSTRATION 4.153

For a reaction, $E_a = 0$ and $k = 3.2 \times 10^4 \text{ s}^{-1}$ at 300 K. The value of k at 310 K would be

a.
$$6.4 \times 10^4 \text{ s}^{-1}$$

b.
$$3.2 \times 10^8 \text{ s}^{-1}$$

$$c. 3.2 \times 10^4 \text{ s}^{-1}$$

d.
$$3.2 \times 10^5 \text{ s}^{-1}$$

Sol.

$$c. \quad k = Ae^{-E_a/RT}$$

When
$$E_a = 0$$
, $k = A$ (constant)

$$k_{310} = k_{300} = 3.2 \times 10^4 \text{ s}^{-1}$$

ILLUSTRATION 4.154

For a gaseous reaction, following data is given:

$$A \to B$$
, $k_1 = 10^{15} e^{-2000/T}$

$$C \to D$$
, $k_2 = 10^{14} e^{-1000/T}$

The temperature at which $k_1 = k_2$ is

Sol.

d. When
$$k_1 = k_2$$

$$10^{15}e^{-2000/T} = 10^{14}e^{-1000/T}$$

$$10 = e^{1000/T} \Rightarrow \ln 10 = \frac{1000}{T}$$

$$\Rightarrow 2.303 \log 10 = \frac{1000}{T}$$

$$T = 434.2 \text{ K}$$

ILLUSTRATION 4.155

For $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + 22$ kcal, E_a for the reaction is 70 kcal. Hence, the activation energy for $2NH_3(g) \longrightarrow N_2(g)$ $+ 3H_2(g)$ is:

- a. 92 kcal
- **b.** 70 kcal
- c. 48 kcal
- d. 22 kcal

Sol.

a.
$$\Delta H = E_{\rm f} - E_{\rm b}$$

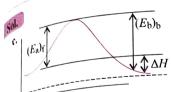
 $-22 = 70 - E_{\rm b}$

$$E_{\rm b} = 92 \text{ keal}$$

ILLUSTRATION 4.156

In an exothermic reaction $X \rightarrow Y$, the activation energy is 100kJ mol⁻¹ of X. The enthalpy of the reaction is -140 kJ mol⁻¹. The activation energy of the reverse reaction $Y \rightarrow X$ is

- a. 40 kJ mol⁻¹
- **b.** 340 kJ mol⁻¹
- c. 240 kJ mol⁻¹
- **d.** 100 kJ mol⁻¹



For X
$$\rightarrow$$
 Y: $(E_a)_f = 100 \text{ kJ mol}^{-1}$
 $\Delta H = -140 \text{ kJ mol}^{-1} = |140 \text{ kJ mol}^{-1}|$
From the figure above $(E_a)_b = (E_a)_f + \Delta H$
 $= 100 + 140 = 240 \text{ kJ mol}^{-1}$

ILLUSTRATION 4.157

The rate constant of a reaction will be equal to the preexponential factor when

- a. Temperature in centigrade is zero.
- b. The absolute temperature is zero.
- c. The absolute temperature is infinity.
- d. No suitable answer.

Sol.

c.
$$k = Ae^{-E_a/RT}$$

(A is called pre-exponential factor)

When
$$T \to \infty$$

$$k = Ae^{-E_a/R\infty}$$

$$k = Ae^0 \left[\frac{-E_a}{R \times \infty} = 0 \right]$$

ILLUSTRATION 4.158

The activation energy for the reaction:

$$2AB \rightarrow A_2(g) + B_2(g)$$

is 159.7 kJ mol⁻¹ at 500 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

(Given:
$$2.3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 500 \text{ K} = 9561.1 \text{ J mol}^{-1}$$
)

Fraction of molecules having energy equal to or greater than activation energy is:

$$E_{a} = \frac{n}{N} = x = e^{-E_{a}/RT}$$

$$\therefore x = e^{-E_a/RT}$$

$$\ln x = \frac{-E_a}{RT} \Rightarrow 2.3 \log x = \frac{-E_a}{RT}$$

or
$$\log x = -\frac{159.7 \times 10^3 \text{ J mol}^{-1}}{2.3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}$$

$$= -\frac{159.7 \times 10^3 \text{ J mol}^{-1}}{9561.1 \text{ J mol}^{-1}} = -16.7$$

$$\therefore x = \text{Antilog}(-16.7)$$
= Antilog(-16 - 0.7 + 1 - 1)
= Antilog(\overline{17}.3)
= 2 \times 10^{-17}

ILLUSTRATION 4.159

A reaction occurs in 'n' parallel path having energy of activation as E, 2E, 3E, nE and rate constants as K, 2K, 3K..... nK respectively. If $E_{Av} = 3E$, then the value of n is:

Sol.
$$E_{Av} = \sum_{n=1}^{i} \frac{nK_i E_i}{K_i} = \frac{E \times K + 2E \times 2K + 3E \times 3K + \dots nE \times nK}{K + 2K + 3K + \dots nK}$$
$$= \frac{[1 + (2)^2 + (3)^2 + \dots (n)^2]KE}{(1 + 2 + 3 + \dots n)K}$$

(Given $E_{Av} = 3E$), For n = 4,

$$E_{Av} = \frac{[1+(2)^2+(3)^2+(4)^2]E}{(1+2+3+4)} = \frac{30E}{10} = 3E$$

Note: If $E_{Av} = 3.66$, then n = 5, if $E_{Av} = 3E$, then n = 4, If $E_{Av} = 2.33 E$, then n = 3, if $E_{Av} = 1.66 E$, then n = 2

ILLUSTRATION 4.160

If the rate of a reaction is 3.2×10^{-2} mol L⁻¹ s⁻¹ at 80° C and 2.0×10^{-3} mol L⁻¹ s⁻¹ at 40° C, then what will be the temperature coefficient of the reaction?

Sol. Since temperature coefficient is the ratio of rate constants or rate of reaction at 35°C and 25°C. i.e., for 10°C or 10 K rise of temperature.

Let temperature coefficient is represented as μ

$$\therefore \frac{r_2}{r_1} = (\mu)^{\Delta T/10}$$
$$\frac{3.2 \times 10^{-2}}{2.0 \times 10^{-3}} = (\mu)^{\left(\frac{80 - 40}{10}\right)}$$

$$16 = (\mu)^{\left(\frac{40}{10}\right)} \Rightarrow (2)^4 = (\mu)^4 \qquad \therefore \ \mu = 2$$

CONCEPT APPLICATION EXERCISE 4.4

- 1. The rate constant for the decomposition of nitrogen pentoxide: $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$ is 3.46×10^{-5} at 25°C and 4.87×10^{-3} at 65°C. Calculate the energy of activation for the reaction.
- 2. For the decomposition of ethyl iodide:

$$C_2H_5I \longrightarrow C_2H_4 + HI$$

the rate constants are 1.60×10^{-5} s⁻¹ and 6.36×10^{-3} at 600 K and 700 K, respectively. Calculate the activation energy for the reaction.

 The rate constant for the decomposition of N₂O₅ at various temperatures is given below:

T (°C)	0	20	40	60	80
$10^5 \times k (s^{-1})$	0.0787	1.70	25.7	178	2140

Draw a graph between $\ln k$ and 1/T and calculate the values of A and E_a .

- **4.** The rate constant of a reaction is 1.2×10^{-3} s⁻¹ at 30°C and 2.1×10^{-3} s⁻¹ at 40°C. Calculate the energy of activation of the reaction.
- 5. A substance decomposes by first order reaction. At 300 K, the decomposition is 50% complete in 20 min. At 350 K, the decomposition of the same substance is 50% complete in 5 min. Calculate the activation energy for the reaction.
- 6. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation for the reaction.
- 7. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if $k = 1.60 \times 10^6 \text{ s}^{-1}$ at 298 K?
- 8. Two reactions of the same order have equal exponential factors but their activation energies differ by 24.9 kJ mol⁻¹. Calculate the ratio between the rate constants of these reactions at 27°C. $(R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1})$.
- 9. A reaction proceeds five times more at 60°C as it does at 30°C. Estimate the energy of activation.
- 10. Calculate the rate constant and half life period for a first order reaction having the activation energy 39.3 kcal mol⁻¹ at 300°C and the frequency constant 1.11×10^{11} s⁻¹.
- 11. The specific rate constant for the decomposition of formic acid is 5.5×10^{-4} s⁻¹ at 413 K. Calculate the specific rate constant at 458 K, if the nergy of activation is 2.37×10^4 cal mol-1.

ANSWERS

- 1. 103.56 kJ mol⁻¹
- 2. 209.1 kJ mol⁻¹
- 3. $E_a = 100.67 \text{ kJ mol}^{-1}$; $A = 1.54 \times 10^{-13} \text{ min}$
- **4.** 44.1 kJ mol⁻¹
- **5.** 24.2 kJ mol^{-1} **6.** $52.80 \text{ kJ mol}^{-1}$
- 7. $k_1 = k_2 = 1.6 \times 10^6 \text{ s}^{-1}$ 8. 2.199×10^6
 - 9.40.02 kJ mol⁻¹

- **10.** $k = 1.4 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 6078 \text{ s}$ **11.** $9.38 \times 10^{-3} \text{ s}^{-1}$

Solved Examples

Rate, Order of Reaction, and Half Life

EXAMPLE 4.1

Which of the following will react fastest (i.e., produce most of the product in a given time) and which will react at the highest rate?

- a. 1 mol of A and 1 mol of B in a 1-L vessel.
- b. 2 mol of A and 2 mol of B in a 2-L vessel.
- c. 0.2 mol of A and 0.2 mol of B in a 0.1-L vessel.

Sol. Fastest (b): Since there are more reactants present, there will be more products produced per unit time.

Highest rate (c): The vessel with greatest concentration will experience the greatest change in concentration per unit time. The greatest change in concentration per unit time is in (c).

In (a),
$$[A] = [B] = \frac{1 \text{ mol}}{1 \text{ L}} = 1 \text{ M}$$

In (b), [A] = [B] =
$$\frac{2 \text{ mol}}{2 \text{ L}}$$
 = 1 M

In (c), [A] = [B] =
$$\frac{0.2 \text{ mol}}{0.1 \text{ L}}$$
 = 2 M

EXAMPLE 4.2

For the reaction,

 $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$, the rate of formation of O_2 is 0.032 g h⁻¹.

- a. Calculate the rate of conversion of N₂O₅ in g h⁻¹.
- b. Calculate the rate of formation of NO₂ in g h⁻¹.
- Sol. Refer Section "Relation Between Rate of Formation," Decomposition".

$$\frac{1}{2} \frac{-d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\mathbf{a.} \quad \therefore \quad \frac{-d[\mathrm{N}_2\mathrm{O}_5]}{dt} = 2 \times \frac{d[\mathrm{O}_2]}{dt} \times \frac{Mw \text{ of } \mathrm{N}_2\mathrm{O}_5 \text{ in g}}{Mw \text{ of } \mathrm{O}_2 \text{ in g}}$$

$$= 2 \times 0.032 \times \frac{98}{32} = 0.196 \text{ g h}^{-1}$$

b.
$$\therefore \frac{d[\text{NO}_2]}{dt} = 4 \times \frac{d[\text{O}_2]}{dt} \times \frac{Mw \text{ of NO}_2 \text{ in g}}{Mw \text{ of O}_2 \text{ in g}}$$
$$= 4 \times 0.032 \times \frac{46}{32} = 0.184 \text{ g h}^{-1}$$

EXAMPLE 4.3

The rate of formation of a dimer in a second order dimerization reaction is 9.5×10^{-5} mol L^{-1} s⁻¹ at 0.01 mol L^{-1} monomer concentration. Calculate the rate constant.

Sol.
$$2A \longrightarrow A_2$$

$$\frac{-d[A]}{2\,dt} = \frac{d[A_2]}{dt}$$

$$\frac{-d[A]}{dt} = \frac{2d[A_2]}{dt}$$
= 2 × 9.5 × 10⁻⁵ mol L⁻¹ s⁻¹
= 1.90 × 10⁻⁴ mol L⁻¹ s⁻¹

Rate =
$$k[A]^2$$

$$1.9 \times 10^{-4} = k[0.01]^2$$

$$k = 1.9 \text{ L mol}^{-1} \text{ s}^{-1}$$

EXAMPLE 4.4

For the decomposition of phosphorus pentachloride at 200°C, it is observed that its pressure falls from 0.15 to 0.10 atm in 25 min. Calculate the average rate of reaction in

- a. atm min-1
- **b.** mol L⁻¹ s⁻¹



$$Rate = \frac{Pressure change}{Time}$$

$$= \frac{0.15 \text{ atm} - 0.10 \text{ atm}}{25 \text{ min}}$$

$$= \frac{0.05 \text{ atm}}{25 \text{ min}} = 0.002 \text{ atm min}^{-1}$$

25 min
b.
$$pV = nRT$$
; $T = 273 + 200$ °C = 473 K

$$\frac{\Delta(n/V)}{\Delta t} \operatorname{mol} L^{-1} \operatorname{min}^{-1} = \frac{\Delta P}{\Delta t} \times \frac{1}{RT}$$

$$= \frac{0.002 \text{ atm min}^{-1}}{(0.082 \text{ L} - \text{atm K}^{-1} \text{ mol}^{-1}) (473 \text{ K})}$$

$$= 5.15 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= 8.58 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$$

EXAMPLE 4.5

Raising the concentration of a particular reactant by a factor of Sincreases the reaction rate 25 times. What is the kinetic order of this reactant?



$$\propto [A]^a$$
 ...(i)

$$25r \propto [5A]^a \qquad ...(ii)$$

Dividing equation (ii) by (i),

$$\frac{25r}{r} \propto \frac{\left[5A\right]^a}{\left[A\right]^a}$$

a = 2, second order reaction

EXAMPLE 4.6

The rate of reaction:

$$H_2O + 2S_2O_4^{2-}(aq) \longrightarrow 2HSO_3^{\circ}(aq) + S_2O_3^{2-}(aq)$$

was studied as follows. In an experiment, the concentration of $\mathbb{S}_2\mathbb{O}_4^{2-}$ (0.4 M) half changed in 3.73 \times 10⁶ s. In another experiment, 0.25 M ${\rm S_2O_4}^{2-}$ half changed in 6.0×10^6 s. Find the order of the reaction.



Sol.
$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2}\right)^{n-1}$$

$$\log \frac{t_2}{t_1} = (n-1)\log \left(\frac{a_1}{a_2}\right)$$

$$\log \frac{6.0 \times 10^6 \text{ s}}{3.73 \times 10^6 \text{ s}} = (n-1) \log \frac{0.4 \text{ M}}{0.25 \text{ M}}$$

$$0.2065 = (n-1)(0.2041)$$

$$(n-1) = \frac{0.2041}{0.2065} = 1 \implies n = 1 + 1 = 2$$

It is a second order reaction.

EXAMPLE 4.7

The experimental data for the decomposition of nitrogen pentoxide in the gaseous phase at 218 K are as follows: $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

Time (s)	$[N_2O_5]$ (mol L ⁻¹)
0	1.63×10^{-2}
400	1.36×10^{-2}
800	1.14×10^{-2}
1200	0.95×10^{-2}
1600	0.79×10^{-2}

Calculate the rates of reaction at the time given above (assuming that the rate remains constant during the intervals given). Also find out the following:

- a. Rate law expression
- b. Rate constant
- c. Order of reaction

Sol.

Sol.			
Time	N ₂ O ₅	Rate = $\frac{N_2O_5}{t}$	$k = \frac{\text{Rate}}{\text{N}_2\text{O}_5}$
(s)	(mol L ⁻¹)	(mol L ⁻¹ s ⁻¹)	(s ⁻¹)
0	1.63×10^{-2}	·	
400	1.36×10^{-2}	$\frac{(1.63 - 1.36) \times 10^{-2}}{400 - 0}$	4.96 × 10 ⁻⁴
		$=6.75\times10^{-6}$	
800	1.14 × 10 ⁻²	$\frac{(1.36 - 1.14) \times 10^{-2}}{800 - 400}$	4.82 × 10 ⁻⁴
		$=5.5\times10^{-6}$	
1200	0.95×10^{-2}	$\frac{(1.14 - 0.95) \times 10^{-2}}{1200 - 800}$	5.00 × 10 ⁻⁴
	ř-	$=4.75\times10^{-6}$	
1600	0.79×10^{-2}	$\frac{(0.95 - 0.79) \times 10^{-2}}{1600 - 1200}$	5.06 × 10 ⁻⁴
		$=4.00\times10^{-6}$	

Since the value of *k* comes out to be nearly constant for the expression rate/N₂O₅, this shows that the rate law expression

Rate =
$$k [N_2O_5]$$

Mean value of $k = 4.96 \times 10^{-4} \text{ s}^{-1}$

EXAMPLE 4.8

The following rate data were obtained at 303 K for the following reaction:

 $2A + B \longrightarrow C + D$

Exp	[A] (mol L ⁻¹)	[B] (mol L ⁻¹)	Initial rate of formation of D	
I	0.1	0.1	$6.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$	
П	0.3	0.2	$7.2 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$	
III	0.3	0.4	2.88 × 10 ⁻¹ mol L ⁻¹ min ⁻¹	
IV	0.4	0.1	$2.4 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$	

What is the rate law? What is the order with respect to each reactant and the overall order? Also calculate the rate constant and write its units.

Sol. From experiment I and IV, it may be noted that [B] is same but [A] has been four times. The rate of reaction also has become four times. This means that order w.r.t. A,

Rate
$$\propto$$
 [A] ...(i)

From experiment II and III, it may be noted that [A] is kept same and [B] has been doubled, the rate of reaction has become four times. This means that order w.r.t. B,

Rate
$$\propto [B]^2$$
 ...(ii)

Combining (i) and (ii), we get the rate law for the given reaction as:

Rate =
$$k$$
 [A] [B]²

Thus, order w.r.t. A = 1, order w.r.t. B = 2, and overall order of the reaction = 1 + 2 = 3.

The rate constant and its units can be calculated from the data of each experiment using the expression

$$k = \frac{\text{Rate}}{[A][B]^2} = \frac{\text{mol } L^{-1} \text{ min}^{-1}}{(\text{mol } L^{-1}) (\text{mol } L^{-1})^2} = \text{mol}^{-2} L^2 \text{ min}^{-1}$$

Experiment	$k \text{ (mol}^{-2} \text{ L}^2 \text{ min}^{-1})$
I	$\frac{6.3 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$
II	$\frac{7.2 \times 10^{-2}}{0.3 \times (0.2)^2} = 6.0$
Ш	$\frac{2.88 \times 10^{-1}}{0.3 \times (0.4)^2} = 6.0$
IV	$\frac{2.4 \times 10^{-2}}{0.4 \times (0.1)^2} = 6.0$

 \therefore Rate constant, $k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$

EXAMPLE 4.9

What is the ratio of $t_{1/2}$ to $t_{1/3}$ (for the amount of substance left) for first order reaction?

Sol. a = Initial amount

$$(a-x) =$$
Amount left

$$t_{1/2} = \frac{2.3}{k} \log \left(\frac{1}{1/2} \right) = \frac{2.3}{k} \log 2$$
 ...(i)

$$t_{1/3} = \frac{2.3}{k} \log \frac{a}{a - x}$$
$$= \frac{2.3}{k} \log \frac{1}{1/3}$$

$$= \frac{2.3}{k} \log 3 \qquad \qquad \dots \text{(ii)}$$

$$\therefore \frac{t_{1/2}}{t_{1/3}} = \frac{(2.3/k) \log 2}{(2.3/k) \log 3} = \frac{0.3}{0.48} = 0.625$$

Alternatively

$$\frac{t_{1/2}}{t_{1/3} \text{ (left)}} = \frac{0.3}{\log\left(\frac{1}{1/3}\right)} = \frac{0.3}{\log 3} = \frac{0.3}{0.48} = 0.625$$

EXAMPLE 4.10

The half life for given reaction was doubled as the initial concentration of a reactant was doubled. What is the order of reaction.

Sol. For *n*th order:

$$(t_{1/2})_1 \propto (a_1)^{1-n}$$

 $(t_{1/2})_2 = 2(t_{1/2})_1$
 $a_2 = 2a_1$

$$\therefore \frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{(a_2)^{1-n}}{(a_1)^{1-n}}$$

$$\frac{2(t_{1/2})_1}{(t_{1/2})_1} = \frac{(2a_1)^{1-n}}{(a_1)^{1-n}}$$

$$(2)^1 = (2)^{1-n}$$

$$1 = 1 - n$$

$$\therefore n = 0$$

Alternatively

Since $t_{1/3}$ becomes doubled when the concentration of ³ reactant is doubled.

$$\therefore \ {\bf t}_{1/2} \propto (a)^{1}$$

which is the equation for zero order.

Hence, OR = 0

EXAMPLE 4.11

Why the term half life is not used for second order reaction?

Sol. For a second order reaction, the time in which half the reactant will be used up is dependent on the initial concentration, in contrast to the situation for a first order reaction. Therefore, the concept of half life is much less useful for second order reaction.

EXAMPLE 4.12 The reaction $SO_2Cl_2 \xrightarrow{k_1} SO_2 + Cl_2$ is a first order reaction $SO_2Cl_2 \xrightarrow{\text{the reaction } SO_2Cl_2} = 2.2 \times 10^{-5} \text{ s}^{-1}$ at 575 K. What percentage of SO_2Cl_2 with $k_1 = 2.2 \times 10^{-5}$ given by the second of SO_2Cl_2 with $k_1 = 2.2 \times 10^{-5}$ given by the second of SO_2Cl_2 with $k_1 = 2.2 \times 10^{-5}$ given by the second of SO_2Cl_2 given by the second with $k_1 = 2.2$ min when the reaction is carried out will get decomposed in 90 min when the reaction is carried out

Since the reaction is of the first order (given)

Since the xiv

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$
 and $k = 2.2 \times 10^{-5} \text{ s}^{-1}$

$$t = 90 \text{ min} = 90 \times 60 = 5400 \text{ s (given)}$$

$$2.2 \times 10^{-5} = \frac{2.303}{5400} \log \frac{a}{a - x}$$

$$or \log \frac{a}{a-x} = 0.0516$$

or
$$\frac{a}{a-x}$$
 = antilog(0.0516) = 1.127

or
$$a = (a - x)1.127$$
 or $a = a(1.127) - x(1.127)$

or
$$0.127a = 1.127x$$

$$\therefore \frac{x}{a} = \frac{0.127}{1.127} = 0.113 = 11.3\%$$

EXAMPLE 4.13

A first order reaction has a specific reaction rate of 10⁻³ s⁻¹. How much time will it take for 10 g of the reactant to reduce to $2.5 \,\mathrm{g}$. (Given $\log 4 = 0.6021$).

Sol. We know that for a first order reaction

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

Here, initial concentration a = 10 g and concentration left after time t = 2.5 g

i.e.,
$$(a - x) = 2.5 g$$
;

Specific reaction constant $k = 10^{-3} \text{ s}^{-1}$

 \therefore Time required for the reactant to reduce to 2.5 g

$$= \frac{2.303}{10^{-3}} \times \log \frac{10}{2.5}$$

$$= \frac{2.303}{10^{-3}} \times \log 4 = \frac{2.303}{10^{-3}} \times 0.6021$$
(Given log 4 = 0.6021)

= 1386.6 s

EXAMPLE 4.14

The esterification of acetic anhydride by ethyl alcohol can be represented by the following balanced equation:

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

When the reaction is carried out in dilute hexane solution, the Tate may be represented by k[a][b]. When ethyl alcohol (B) is the solvent, the rate may be represented by k[A] (the values of k are not the same in the two cases). Explain the difference in the apparent order of the reaction.

Sol. When a solvent is also a reactant, its concentration is so large compared with the extent of reaction that it does not change. (Compare the convention we used, in studying the thermodynamics of aqueous solutions, of viewing water as always being in its standard state in all dilute solutions.) Thus, the dependence of the rate on the concentration of ethyl alcohol cannot be determined unless ethyl alcohol becomes a solute in some other solvent so that its concentration can be varied.

EXAMPLE 4.15

An optically active drug has one chiral centre and only dextro rotatory isomer is effective. Moreover, it becomes ineffective when its optical activity is reduced to 35% of original. It was found that mutarotation of this drug was first order reaction with a rate constant of 1×10^{-8} s⁻¹. Find the expiration time of the drug in years.

Sol. The optical activity remained = 35%

So 65% optical activity has been lost

It means 35% of dextro rotatory isomer has been converted to laevo rotatory isomer.

Applying integrated rate law for first order reaction

$$2.303 \log \frac{100}{65} = 1 \times 10^{-18} \times t$$

$$t = 4.31 \times 10^7 \text{ s}$$

$$= 1.37$$
 years

EXAMPLE 4.16

A radioactive element ($t_{1/2} = 50$ days) is spread over a room. Its activity is 30 times the permissible value for safe working. Calculate the number of days after which the room will be available for safe working.

Sol.
$$r_0 = 30r$$

where r is the activity for safe working

$$t = \frac{2.303}{k} \log \frac{r_0}{r} \ (r_0 \propto N_0 \text{ and } r \propto N)$$

$$t = \frac{2.303 \times 50}{0.693} \log \frac{30r}{r} \qquad \left(\because k = \frac{0.693}{t_{1/2}}\right)$$

$$= 245.44 \text{ days}$$

EXAMPLE 4.17

 $_{84}$ Po²¹⁸ ($t_{1/2}$ = 3.05 min) decays to $_{82}$ Pb²¹⁴ ($t_{1/2}$ = 2.68 min) by α emission while Pb²¹⁴ is a β-emitter. In an experiment starting with 1 g atom of pure Po²¹⁸, how much time would be required for the concentration of Pb214 to reach maximum?

Sol.
$$_{84}Po^{218} \xrightarrow{-\alpha} {_{82}Pb^{214}} \xrightarrow{-\beta} {_{83}Bi^{214}}$$

$$m_0 = 1$$
 g atom = 1 mol

Time at which 82Pb214 is maximum

$$t_{\text{max}} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} = \frac{2.303}{k_1 - k_2} \log \frac{k_1}{k_2}$$

$$k_1 = \frac{0.693}{3.05} = 0.2287$$

$$k_2 = \frac{0.693}{2.68} = 0.258$$

$$t = \frac{2.303}{0.2287 - 0.258} \log \frac{0.2287}{0.258}$$

=4.1 min

EXAMPLE 4.18

The complex [Co(NH₃)₅F]²⁺ reacts with water according to

the equation
$$[Co(NH_3)_5F]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + F^{\odot} \text{ and}$$

Rate = k [Complex] a [H $^{\oplus}$] b

The reaction is acid catalyzed, i.e., [H[®]] does not change during the reaction.

Thus, rate = k' [Complex]³, where k' = k [H^{\oplus}]^b

Calculate a and b from the following data ($t = 25^{\circ}$ C)

ilculate a and t		()	t _{3/4} (hr)
[Complex]	[H [⊕]]	t _{1/2} (hr)	1
	0.01 M	1	1 177
0.1 M	0.02 M	0.5	2
0.2 M	0.02 M		

Rate = k' [Complex]^a; $k' = k[H^{\oplus}]^b$

Since $t_{3/4} = 2t_{1/2}$

Hence, order w.r.t. complex, a = 1.

Now,
$$k_1 = k [H^{\oplus}]_1^b$$
; $k'_2 = k [H^{\oplus}]_2^b$

$$\therefore \ \frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{[\mathbf{H}^{\oplus}]_1}{[\mathbf{H}^{\oplus}]_2}\right)^b$$

$$\frac{0.5}{1} = \left(\frac{0.01}{0.02}\right)^b \Rightarrow b = 1$$

Hence, order w.r.t. $\lceil H^{\oplus} \rceil = 1$

EXAMPLE 4.19

For the reaction

$$[\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_4\operatorname{Cl}_2]^{\oplus}(\operatorname{aq}) \xrightarrow{k_1} [\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_5\operatorname{Cl}]^{2+}(\operatorname{aq}) \xrightarrow{k_2} [\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_6]^{3+}(\operatorname{aq})$$

 $k_1 = 1.78 \times 10^{-3} \,\mathrm{s}^{-1}$ and $k_2 = 5.8 \times 10^{-5} \,\mathrm{s}^{-1}$ for

the initial concentration of [Cr(H₂O)₄Cl₂][⊕] is 0.0174 mol L⁻¹ at 0°C. Calculate the value of time at which the concentration of [Cr(H₂O)₅Cl]²⁺ is maximum.

The time required for two consecutive reactions to react its maximum activity or concentration is given by

$$t = \frac{2.303 (\log k_1 - \log k_2)}{k_1 - k_2}$$

$$= \frac{2.303 (\log 1.78 \times 10^{-3} - \log 5.8 \times 10^{-5})}{1.78 \times 10^{-3} - 5.8 \times 10^{-5}}$$

$$= 1990 \text{ s.}$$

EXAMPLE 4.20 Substance A isomerizes according to a first order rate law with $k = 5.0 \times 10^{-5} \,\mathrm{s}^{-1}$

- a. If the initial concentration of A is 1.00 M, what is the initial
- b. What is the rate after 1.00 hr?

a. Rate =
$$k$$
 [A] = $(5.0 \times 10^{-5} \text{ s}^{-1}) (1.00 \text{ M})$
= $5.0 \times 10^{-5} \text{ M s}^{-1}$

b.
$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

 $5 \times 10^{-5} \text{ s}^{-1} = \frac{2.303}{3600 \text{ s}} \log \frac{1}{a - x} \quad (a - x = c_t)$
 $5 \times 10^{-5} \times 3600 = 2.303 \log \frac{1}{c_t}$

$$\frac{0.18}{2.303} = \log \frac{1}{c_t}$$

$$\log c_t = 0.0783$$

$$(a-x) = [c_t] = 0.835 \text{ M}$$

Rate =
$$k[a-x]$$

$$= 5.0 \times 10^{-5} \times 0.835 = 4.2 \times 10^{-5} \,\mathrm{M \, s^{-1}}$$

EXAMPLE 4.21

reactant with $k = 5.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A was 0.1 M and that of B was 6.0 M. State any approximation made in obtaining your result.

Sol. Since [B] = 6.0 M, we can consider that its concentration remains constant throughout. Thus,

Rate =
$$k$$
 [A] [B]
= k [A] × 6 M = 6 k [A]
= k' [A]

where k' (= 6k) is new constant and reaction under this condition is supposed to follow first order kinetics.

$$k' = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$\log \frac{a}{a-x} = \frac{k't}{2.303} = \frac{6kt}{2.303}$$

$$\log \frac{a}{a-x} = \frac{6 \times 5.0 \times 10^{-3} \times 100}{2.303} = 1.3026$$

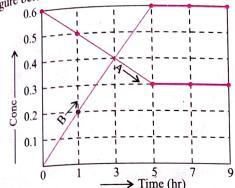
$$\left(\frac{a}{a-x}\right)=20$$

$$\frac{a-x}{a}=\frac{1}{20}$$

$$(a-x) = \frac{a}{20} = \frac{0.1}{20} = 0.005 \text{ M}$$

Hence, the concentration of reactant A after 100 s is 0.005 M.

EXAMPLE 4.22 The progress of the reaction $A \longrightarrow nB$, with times is presented to the progress below. in the figure below.



Determine:

- a. The value of n
- **b.** $K_{\rm eq}$
- c. Initial rate of conversion of A

In the given time of 4 hr (1 to 5), concentration of A falls from 0.5 to 0.3 M, while in the same time concentration of B increases from 0.2 to 0.6 M. The increase in the concentration of B in a given time is twice the decrease in the concentration of A.

a. Thus, n=2

b.
$$\frac{[B_{eq}]^2}{[A]_{eq}} = \frac{(0.6)^2}{0.3} = 1.2$$

c. Initial rate of conversion of A = $\frac{0.6 - 0.5}{1.00}$ = 0.1 M hr⁻¹

EXAMPLE 4.23

At constant temperature and constant pH of 4, the inversion of sucrose proceeds with a constant half life of 300 min. At the same temperature but at pH of 3 the half life is constant at 30 min. Calculate the order of reaction w.r.t. sucrose and w.r.t. [H[®]].

Sol. Sucrose [A] +
$$H_2O \xrightarrow{H^{\oplus}} Glucose + Fructose$$

$$\frac{-d[A]}{dt} = \text{Rate} = k[A]^a[H^{\oplus}]^b$$

(Does not depend on H2O, since it is in large excess)

During any experiment, pH is constant, hence

$$\frac{-d[A]}{dt} = k'[A]^a, \text{ where } k' = k [H^{\oplus}]^b$$

Since half life is independent of the initial concentration of a, hence a = 1, consequently k', is a first order rate constant and is given by

$$k' = \frac{0.0693}{t_{1/2}}$$

$$\therefore \frac{(t_{50})_1}{(t_{50})_2} = \frac{k'_2}{k'_1} = \frac{k [H^{\oplus}]_2^b}{k [H^{\oplus}]_1^b} = \frac{[H^{\oplus}]_2^b}{[H^{\oplus}]_1^b}$$

$$\left(\frac{300}{30}\right) = \left(\frac{10^{-3}}{10^{-4}}\right)^b \text{ or } b = 1$$

Therefore, the rate of hydrolysis of sucrose has a first order dependence on $[H^{\oplus}]$, so that

$$\frac{-d[A]}{dt} = k[A][H^{\oplus}]$$

 \therefore Order w.r.t sucrose = 1; order w.r.t [H^{\operatorname{\text{\text{\$}}}] = 1}

Mechanism of Reaction

EXAMPLE 4.24

In a certain polluted atmosphere containing O₃ at a steady-state concentration of 2.0×10^{-8} mol L⁻¹, the hourly production of O₃ by all sources was estimated as 7.2×10^{-15} mol L⁻¹. If the only mechanism for the destruction of O₂ is the second order reaction,

$$2O_3 \longrightarrow 3O_2$$

Calculate the rate constant for the destruction reaction defined by the rate law for $-\Delta[O_3]/\Delta t$.

Sol. At the steady state, the rate of destruction of O₃ must be equal to the rate of its generation, 7.2×10^{-15} mol L⁻¹ hr^{-1} .

For the second order rate law:

$$k = -\frac{1}{[O_3]^2} \frac{\Delta[O_3]}{\Delta t}$$

$$= \frac{1}{(2.0 \times 10^{-8} \text{M})^2} \times \frac{7.2 \times 10^{-15} \text{M hr}^{-1}}{3600 \text{ s hr}^{-1}}$$

$$= 5 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

EXAMPLE 4.25

Write a rate expression for each species. Assuming [B] is constant, write a rate expression for [A] and [C] so that they do not contain [B] term. Under what conditions will the reaction be pseudo first order to second order?

Mechanism of reaction is

$$A \xrightarrow{k_1 \atop k_2} B$$

$$B + A \xrightarrow{k_3} C$$

$$2A \longrightarrow C$$

Sol. The rate expression are:

$$\frac{-d[A]}{dt} = k_1[A] - k_2[B] + k_3[B][A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[A][B]$$

$$\frac{d[C]}{dt} = k_3[A][B]$$

Using the steady state approximation for [B], i.e.,

$$\frac{d[B]}{dt} = 0$$
 and solving for [B], gives

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[A][B] = 0$$

[B] =
$$\frac{k_1[A]}{k_2 + k_3[A]}$$

Substituting this expression for [B] into the expression for

$$\frac{-d[A]}{dt}$$
 and $\frac{d[C]}{dt}$ gives

$$\frac{-d[A]}{dt} = k_1[A] - k_2 \frac{k_1[A]}{k_2 + k_3[A]} + k_3 \frac{k_1[A]}{k_2 + k_3[A]}[A]$$

$$= \frac{2k_1k_3[A]^2}{k_2 + k_3[A]}$$
$$\frac{d[C]}{dt} = k_3[A] \frac{k_1[A]}{k_2 + k_3[A]} = \frac{k_1k_3[A]^2}{k_2 + k_3[A]}$$

Note that $\frac{-d[A]}{dt} = 2\left[\frac{d[C]}{dt}\right]$. If $k_3[A] >> k_2$, then condition

for pseudo first order

$$\frac{d[C]}{dt} = \frac{k_1 k_3 [A]^2}{k_3 [A]} = k_1 [A]$$

and if $k_3[A] \ll k_2$, then condition for pseudo second order

$$\frac{d\left[C\right]}{dt} = \frac{k_1 k_3 [A]^2}{k_2}$$

EXAMPLE 4.26

Consider the following proposed mechanism

$$A \stackrel{k_1}{\longleftarrow} B$$
, $B + C \stackrel{k_3}{\longrightarrow} D$

For the overall reaction $A + C \longrightarrow D$, assuming B to be an intermediate described by the steady state approximation, write the rate expression for [A].

Sol. Applying steady state approximately for [B], gives

$$\frac{d[\mathbf{B}]}{dt} = k_1[\mathbf{A}] - k_2[\mathbf{B}] - k_3[\mathbf{B}][\mathbf{C}] = 0$$

[B] =
$$\frac{k_1[A]}{k_2 + k_3[C]}$$

Writing the rate expression for [A] and substituting the expression for [B] gives

$$\frac{-d[A]}{dt} = k_1[A] - k_2[B] = k_1[A] - k_2 \frac{k_1[A]}{k_2 + k_3[C]}$$
$$= \frac{k_1 k_3[A][C]}{k_2 + k_3[C]}$$

EXAMPLE 4.27

Consider the following proposed mechanism:

$$A_2 \Longrightarrow 2A (k_1)$$

$$A + B \Longrightarrow C (k_2)$$

$$A_2 + C \longrightarrow D + A (k)$$

For the overall chemical equation $A_2+B \longrightarrow D$, assuming that the equilibria are rapidly established in the first two steps, write the rate expression for [D].

Sol. From the equilibria steps,

$$[A] = [k_1 [A_2]]^{1/2}$$

[C] =
$$k_2[A][B] = k_2k_1[A_2]^{1/2}[B] = k_1^{1/2}k_2[A_2]^{1/2}[B]$$

Substituting these expressions for [A] and [C] into the rate expression for [D] gives

$$\frac{d[D]}{dt} = k[A_2][C] = k[A_2] k_1^{1/2} k_2[A_2]^{1/2}[B]$$
$$= kk_1^{1/2} k_2[A_2]^{3/2}[B]$$

EXAMPLE 4.28

Consider the following mechanisms:

$$A_2 \rightleftharpoons 2A(k)$$

$$A+B_2 \xrightarrow{k_1} C+B$$
 $B+A_2 \xrightarrow{k_2} C+A$

For the overall chemical equation $A_2 + B_2 \longrightarrow 2C$.

Assuming that the equilibrium is rapidly established and the steady state approximation is valid for [B], write the rate expression for [C].

Sol. From the equilibrium step:

 $[A] = k^{1/2} [A_2]^{1/2}$, applying steady state approximation for [B] gives

$$\frac{d[B]}{dt} = k_1[A][B_2] - k_2[B][A_2] = 0$$

[B] =
$$\frac{k_1[A][B_2]}{k_2[A_2]} = \frac{k_1k^{1/2}[A_2]^{1/2}[B]}{k_2[A_2]}$$

The rate expression for [C] is

$$\begin{split} \frac{d[\mathbf{C}]}{dt} &= k_1[\mathbf{A}][\mathbf{B}_2] + k_2[\mathbf{B}][\mathbf{A}_2] \\ &= k_1 k^{1/2} [\mathbf{A}_2]^{1/2} [\mathbf{B}_2] + \frac{k_1 k_2 k^{1/2} [\mathbf{A}_2]^{1/2} [\mathbf{B}_2]}{k_2 [\mathbf{A}_2]^2} \\ &= 2k_1 k^{1/2} [\mathbf{A}_2]^{1/2} [\mathbf{B}_2] \end{split}$$

EXAMPLE 4.29

The rate equation for the overall equation is:

$$H_3AsO_4(aq) + 2H^{\oplus}(aq) + 3I^{\odot}(aq) \stackrel{k_f}{\rightleftharpoons} H_3AsO_3(aq) + I_3^{\odot}(eq) + H_2O(l)$$

$$\frac{d[I_3^{\odot}]}{dt} = k_f [H_3 AsO_4] [I^{\odot}] [H^{\oplus}] - k_f \frac{[H_3 AsO_3] [I^{\odot}_3]}{[I^{\odot}]^2 [H^{\oplus}]}$$

where $k_f = 4.7 \times 10^{-4} L^2 \text{ mol}^{-2} \text{ min}^{-1}$ and

$$k_r = 3 \times 10^{-3} \text{ mol}^2 \text{ L}^{-2} \text{ min}^{-1}$$

Determine the equilibrium constant for this reaction from the rate constants.

Sol.
$$\frac{d[I_3^{\odot}]}{dt} = k_{\mathrm{f}}[H_3 \text{AsO}_4] [I^{\odot}] [H^{\oplus}] - k_{\mathrm{r}} \frac{[H_3 \text{AsO}_3][I^{\odot}_3]}{[I^{\odot}]^2 [H^{\oplus}]} = 0$$

$$k = \frac{[H_3 As O_3][I_3^{\circ}]}{[H_3 As O_3][I^{\circ}]^3 [H^{\oplus}]^2}$$
$$= \frac{k_f}{k_h} = \frac{4.7 \times 10^{-4}}{3 \times 10^{-3}} = 0.156$$

EXAMPLE 4.31

$$H_2(g) + Ar(g) \xrightarrow{k_{\rm f}} 2H(g) + Ar(g)$$
 $k_{\rm f} = 2.2 \times 10^4 \, \text{L mol}^{-1} \, \text{s}^{-1} \, \text{and} \, k_{\rm c} = 1.02 \times 10^{-4} \, \text{at } 3000 \, \text{K.}$ What is the value of $k_{\rm r}$?

Sol.
$$k_c = k_l/k_r$$

$$k_r = \frac{2.2 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}}{1.02 \times 10^{-4} \text{ mol L}^{-1}} = 2.15 \times 10^8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

EXAMPLE 4.31

Consider parallel reactions:

$$A \xrightarrow{k_1} B$$
, $2A \xrightarrow{k_2} C + D$

What would be the rate expression for [A]?

Sol. The rate expression for [A] is:

$$\frac{-d[A]}{dt} = k_1[A] + 2k_2[A]^2$$

EXAMPLE 4.32

Consider a mechanism in which a single reactant produces several products by the following parallel first order reactions:

$$A \xrightarrow{k_1} B$$
, $A \xrightarrow{k_2} C$ $A \xrightarrow{k_3} D$

Write the rate expression for [A].

Sol.
$$\frac{-d[A]}{dt} = k_1[A] + k_2[A] + k_3[A]$$

= $(k_1 + k_2 + k_3)[A]$
= $k[A]$

EXAMPLE 4.33

A proposed mechanism for reaction $A \longrightarrow B$ is

$$A \xrightarrow{k_1 \atop k_2} C \qquad \qquad C \xrightarrow{k_3 \atop k_4} B$$

Determine the expression for the equilibrium constant for the overall reaction in terms of the rate constants.

$$k = \frac{[C]}{[A]} = \frac{k_1}{k_2}$$
 $k' = \frac{[B]}{[C]} = \frac{k_3}{k_4}$

Solving first equation and substituting into the second equation gives:

$$\frac{[\mathrm{B}]}{[\mathrm{A}]\left(\frac{k_1}{k_2}\right)} = \frac{k_3}{k_4}$$

Overall equilibrium constant is given by:

$$\frac{[\mathbf{B}]}{[\mathbf{A}]} = \left(\frac{k_3}{k_4}\right) \left(\frac{k_1}{k_2}\right)$$

EXAMPLE 4.34

Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexene was measured as 1.26 × 10⁻⁴ s⁻¹ and for the formation of methyl cyclopentene the rate constant was 3.8×10^{-5} s⁻¹. What is the percentage distribution of the rearrangement products?

Sol.

∴ Percentage of methylcyclopentene = 23%

EXAMPLE 4.35

Trans-1,2-dideuterocyclopropane (A) undergoes a first order decomposition. The observed rate constant at a certain temperature, measured in terms of disappearance of A was 1.52 \times 10⁻⁴ s⁻¹. The analysis of products showed that the reaction followed two parallel paths, one leading to dideuteropropane (B) and the other to cis-1, 2-dideuterocyclopropane (C). (B) was found to constitute 11.2% of the reaction product, independently of the extent of reaction. What is the order of reaction for each path and what is the value of the rate constant for the formation of each of the products?

Sol. In case of parallel path reaction.

$$k_{\rm B} = k_{\rm A} \times \text{Fractional yield of B}$$

 $= 1.52 \times 10^{-4} \times 0.112 = 1.7 \times 10^{-5} \text{ s}^{-1}$
 $k_{\rm C} = k_{\rm A} \times \text{Fractional yield of C}$
 $= 1.52 \times 10^{-4} \times 0.888 = 1.35 \times 10^{-4} \text{ s}^{-1}$

The reaction will be first order for each individual path.

Typical First Order Gas Phase Reactions

EXAMPLE 4.36

The decomposition of Cl₂O₇ at 400 K in gas phase to Cl₂ and O_2 is a first order reaction.

- a. After 55 s at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate k.
- **b.** Calculate the pressure of Cl_2O_7 after 100 s of decomposition.

Sol.

a. $a \propto 0.062 \ (a - x) \propto 0.044$

$$k = \frac{2.303}{55} \log \frac{0.062}{0.044}$$
$$= \frac{2.303}{55} \times 0.1489 = 6.23 \times 10^{-3} \text{ s}^{-1}$$

b.
$$t = 100 \text{ s}, (a - x) \propto P$$

$$\therefore 6.23 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.062}{P}$$

$$P = 0.033 \text{ atm}$$

EXAMPLE 4.37

Ethylene is produced by

$$C_4H_8$$
(cyclobutane) $\xrightarrow{\Delta} 2C_2H_4$

The rate constant is 2.48×10^{-4} s⁻¹. In what time will the molar ratio of the ethylene to cyclobutane in reaction mixture attain the value (a) 1 and (b) 100?

Sol.

$$\begin{array}{ccc}
C_4 H_8 & \xrightarrow{\Delta} & 2C_2 H_4 \\
t = 0 & a & 0 \\
t = t & a - x & 2x
\end{array}$$

a.
$$\frac{2x}{a-x} = 1$$
, $x = \frac{a}{3}$

$$t = \frac{2.303}{k} \log \frac{a}{a - (a/3)}$$
$$= \frac{2.303}{2.48 \times 10^{-4}} \log \frac{3}{2} = 1635.2 \text{ s} = 27.25 \text{ min}$$

b.
$$\frac{2x}{a-x} = 100, \quad x = \frac{100a}{102}$$

$$t = \frac{2.303}{2.48 \times 10^{-4}} \log \left(\frac{a}{a - \frac{100a}{102}} \right)$$

$$= 15856.9 \text{ s} = 264.2 \text{ min}$$

Analysis of Some Important First Order Reactions

EXAMPLE 4.38

From the following data for the decomposition of N_2O_5 in carbon tertrachloride solution at 321 K, show that the reaction is of the first order and calculate the rate constant.

Time (in min) evolved	10	15	20	25	∞
Volume of O ₂ (mL)	6.30	8.95	11.40	13.50	34.75

Sol. If the reaction is of the first order, it must obey the equation.

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_{\infty}}$$

Note: It is a case of direct estimation of one of the product

In the present case, we are given that $V_{\infty} = 34.75 \text{ cm}^3$. The value of k at each instant can be calculated as follows:

Time (min)	V_t	$V_{\infty} - V_t$	$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_{t}}$
10	6.30	34.75 - 6.30 $= 28.45$	$k = \frac{2.303}{10} \log \frac{34.75}{28.45}$ $= 0.01997$
15	8.95	34.75 - 8.95 $= 25.80$	$k = \frac{2.303}{15} \log \frac{34.75}{25.80}$ $= 0.01985$
20	11.40	34.75 - 11.40 $= 23.35$	$k = \frac{2.303}{20} \log \frac{34.75}{23.35}$ $= 0.01987$
25	13.50	34.75 – 13.50 = 21.25	$k = \frac{2.303}{25} \log \frac{34.75}{21.35}$ $= 0.01967$

Thus, the value of k comes out to be nearly constant, hence it is a reaction of the first order.

EXAMPLE 4.39

1.0 mL of ethyl acetate was added to 25 mL of N/2 HCl, 2 mL of the mixture were withdrawn from time to time during the progress of the hydrolysis of the ester and titrated against standard NaOH solution. The amount of NaOH required for titration at various intervals is given below:

Time (min)	0	20	75	119	183	00
NaOH used	20.24	21.73	25.20	27.60	30.22	43.95
(mL)						

The value at ∞ time was obtained by completing the hydrolysis on boiling. Show that it is a reaction of the first order and find the average value of the velocity constant.

Sol. Amount of NaOH used at t = 0

 $(V_0) \propto HCl$ present

Amount of NaOH used at any time t = t,

 $(V_{r}) \propto \text{HCl present} + \text{CH}_{3}\text{COOH formed}$.

CH₃COOH formed at any time, $t = \infty$

Ethyl acetate reacted = $(V_1 - V_0) \propto x$.

Amount of NaOH used at time $t = \infty$

 $(V_{\infty}) \propto \text{HCl present} + \text{Maximum CH}_3\text{COOH formed}$

Maximum CH₃COOH formed \propto Initial concentration of ethyl acetate $(V_{\infty} - V_0) \propto a$

Hence, if the given reaction is of the first order, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

In the present case, $V_0 = 20.24 \text{ mL}$, $V_{\infty} = 43.95 \text{ mL}$

 $V_{\infty} - V_{0} = 43.95 - 20.24 = 23.71 \text{ mL}$ The value of k at different instants can be calculated as

(min)	V_t	$V_{\infty} - V_t$	$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$
20	21.73	43.95 - 21.73 $= 22.22$	$k = \frac{2.303}{20} \log \frac{23.71}{22.22}$ $= 0.00324$
75	25.20	43.95 – 25.20 = 18.75	$k = \frac{2.303}{20} \log \frac{23.71}{22.22}$ $= 0.00313$
119	27.60	43.95 – 27.60 = 16.35	$k = \frac{2.303}{75} \log \frac{23.72}{18.75}$ $= 0.003$
183	30.22	43.95 – 30.22 = 13.73	$k = \frac{2.303}{119} \log \frac{23.71}{16.35}$ $= 0.00299$

Since the value of k comes out to be nearly constant, it is a reaction of first order. The value of $k = 0.00312 \text{ min}^{-1}$.

EXAMPLE 4.40

The inversion of cane sugar was studied in HCl at 298 K. The following polarimetric readings were obtained at different intervals of time:

Time (min)	1	7.18	18.00	27.05	∞
Reading	+24.09	+21.41	+17.74	+15.00	-10.74
(degree)				1 - 222	lor reaction

Show that the inversion of cane sugar is a unimolecular reaction.

In the present case, $r_0 = +24.09$, $r_\infty = -10.74$ $\therefore r_0 - r_\infty = +24.09 - (-10.74) = 34.83$

The value of k at different instants may be calculated as under:

unuci.			$2.203 \qquad r_0 - r_{\infty}$
t (min)	r_t	$r_t - r_{\infty}$	$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$
			2.303 127 34.83
7.18	+21.41	21.41-(-10.74)	$k = \frac{2.303}{7.18} \log \frac{34.83}{31.15}$
		= 32.15	= 0.0116
			$2.303 \log \frac{34.83}{100}$
18.00	+17.74	17.74 - (-10.74)	$k = \frac{2.303}{18.00} \log \frac{34.83}{28.48}$ $= 0.0118$
		= 28.48	= 0.0118
		20,	2 303 . 34.83
27.05	+15.00	15.00 - (-10.74)	$k = \frac{2.303}{27.05} \log \frac{34.83}{25.74}$ $= 0.0109$
1767		= 25.74	
		20	that the reaction

The constancy in the value of k proves that the reaction is of the first order.

Temperature Dependence of a Reaction, Energy of Activation, and Arrhenius Equation

EXAMPLE 4.41

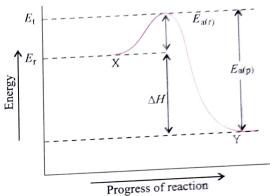
An exothermic reaction X ----- Y has an activation energy of 90 kJ mol-1 of X and the heat of reaction is 250 kJ. Find the activation energy of the reaction $Y \rightarrow X$.

Sol. Since the reaction is exothermic, $E_{a(p)} \ge E_{a(r)}$, so the activation energy diagram will be as shown in Figure below. Energy of activation for the reaction: Y - X

Energy of activation for
$$E_{a(p)} = E_{a(r)} + \Delta H = 90 + 250 = 340 \text{ kJ}$$

Remember that for reaction with

$$n_{\rm p} = n_{\rm r} \left(\Delta H = \Delta U \right)$$

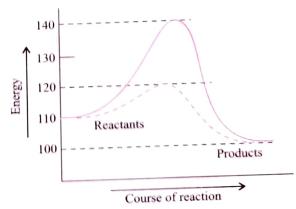


Activation energy diagram for the given problem

EXAMPLE 4.42

Refer picture given below.

- a. Calculate ΔH for the reaction and the energy of activation for the forward reaction as well as backward reaction.
- b. The dotted curve is in the presence of a catalyst. What is the energy of activation for the two reactions in the presence of catalyst?
- c. Will the catalyst change the extent of reaction?



Sol.

a.
$$\Delta H = E_{a(p)} - E_{a(r)} = 100 - 110 = -10 \text{ kJ}$$

From the given picture, in the absence of catalyst, Energy

of activation for the forward reaction

$$= 140 - 110 = 30 \text{ kJ}$$

Energy of activation for the backward reaction = 140 - 100 = 40 kJ

- b. In the presence of catalyst,
 Energy of activation for the forward reaction
 = 120 110 = 10 kJ
 Energy of activation for the backward reaction
 = 120 100 = 20 kJ
- c. No

EXAMPLE 4.43

Calculate the activation energy of a reaction whose reaction rate at 300 K double for 10 K rise in temperature.

Sol. Given, when
$$T_1 = 300 \text{ K}$$
, $k_1 = k \text{ (say)}$
When $T_2 = 300 + 10 = 310 \text{ k}$, $k_2 = 2k$

Substituting these values in the equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$
We get, $\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left(\frac{310 - 300}{300 \times 310} \right)$
or $\log 2 = \frac{E_a \times 10^3}{2.303 \times 8.314} \times \left(\frac{10}{300 \times 310} \right)$

$$E_a = 53.6 \text{ kJ mol}^{-1}$$

EXAMPLE 4.44

The activation energy of a reaction is $94.14 \text{ kJ mol}^{-1}$ and the value of rate constant at 313 K is $18 \times 10^{-5} \text{ s}^{-1}$. Calculate the frequency factor or pre-exponential factor, A.

Sol. Given,
$$E_a = 94.14 \text{ kJ mol}^{-1} = 94140 \text{ J mol}^{-1}$$
;
 $T = 313 \text{ K}$; $k = 1.8 \times 10^{-5} \text{ s}^{-1}$
or $\log k = \frac{-E_a}{2.303RT} + \log A$
 $\log A = \log(1.8 \times 10^{-5}) + \frac{94140}{2.303 \times 8.314 \times 313}$
 $= 25.33 - 5 + 15.7082 = 10.9635$
 $A = \text{antilog}(10.9635) = 9.194 \times 10^{10} \text{ collision s}^{-1}$

EXAMPLE 4.45

The rate constant of a reaction is $1.5 \times 10^7 \,\mathrm{s^{-1}}$ at 50°C and 4.5 $\times 10^7 \,\mathrm{s^{-1}}$ at 100°C. Evaluate the Arrhenius parameters A and E_a .

Sol. The Arrhenius equation is $k = A \exp(-E_a/RT)$ For the two temperatures, we get

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting the given data, we get

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{(2.303) (8.314 \,\mathrm{J \, K^{-1} \, mol^{-1}})} \left(\frac{1}{373 \,\mathrm{K}} - \frac{1}{323 \,\mathrm{K}}\right)$$

or
$$E_{\rm a} = \frac{(2.303)(8.314)(373)(323)}{50} \log (3.0)$$

= 22012.7 J mol⁻¹ = 22.013 kJ mol⁻¹
The value of A would be
 $A = k \exp(E_{\rm a}/RT)$
= $(1.5 \times 10^7 \text{ s}^{-1}) \exp\left[\frac{220127 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(323 \text{ K})}\right]$
= $(1.5 \times 10^7 \text{ s}^{-1})(3630.44) = 5.45 \times 10^{10} \text{ s}^{-1}$

EXAMPLE 4.46

For two reactions (i) P \longrightarrow Product and (ii) Q \longrightarrow Product, the order of reaction (i) is 1 while that of reaction (ii) is 2. At 347 K, the energy of activation of reaction (i) is 55 kJ mol^{-1} but whenever this reaction is carried out in the presence of catalyst at the same temperature, the energy of activation is 53 kJ mol^{-1} . Moreover, for reaction (ii), when the temperature is increased from 298 K to 308 K, the rate of reaction increases as many times as for reaction (i) in the presence of catalyst. Calculate the rate constant of reaction (ii) at 318 K, if the pre-exponential factor for reaction (ii) is $3.56 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$.

Note: Arrhenius equation does not depend on the order of reaction.

Sol.

- a. For reaction (i) P \longrightarrow Product, $k_1 = Ae^{-E_1/RT}$ [In absence of catalyst] $k_2 = Ae^{-E_2/RT}$ [In presence of catalyst] $\therefore \ln \frac{k_2}{k_1} = \frac{(E_2 - E_1)}{RT}$ $= \frac{(55 - 53) \text{ kJ mol}^{-1}}{8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \times 347 \text{ K}}$ = 0.694 $\therefore 2.303 \log \frac{k_2}{k_1} = 0.694$ $\log \frac{k_2}{k_1} = \frac{0.694}{2.303} \approx 0.3$ $\therefore \frac{k_2}{k_1} = 2 \qquad ...(i)$
 - $\log\left(\frac{k_{308}}{k_{208}}\right) = \frac{E_{a}}{2.303R} \left[\frac{T_{2} T_{1}}{T_{1}T_{2}}\right] \qquad ...(ii)$

b. For reaction (ii) $Q \longrightarrow Product$

$$\therefore \frac{k_{308}}{k_{298}} = \frac{k_2}{k_1} = 2 \text{ (Also temperature coefficient is 2)}$$

Substitute the value of k_{308}/k_{298} in Eq. (ii),

$$\therefore \log 2 = \frac{E_{\rm a}}{2.303 \times 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}} \times \frac{10}{298 \times 30}$$

Solve for
$$E_a$$
:

$$E_a = 68.127 \text{ kJ mol}^{-1}$$

$$E_a = 68.127 \text{ kJ mol}^{-1}$$

$$Given: A = 3.56 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}; T = 318 \text{ K}$$

$$Given: A = \frac{E_a}{2.303RT}$$

$$\log k = \log A \qquad 2.303RT$$

$$\log k = \log(3.56 \times 10^9) - \frac{68.127 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 318}$$

Solve for
$$k$$
:

$$k = 7.33 \text{ mol}^{-1} \text{ L s}^{-1}$$

EXAMPLE 4.47

For two first order reactions having same concentration of A For the a b at t = 0, use the given data to calculate the temperature at which both occur with same rate.

Reaction I:
$$A \longrightarrow Z$$
;

$$k_1 = 10^{16} e^{\left(-\frac{3000}{T}\right)}$$

$$\underset{\text{Reaction II:}}{\text{Reaction II:}} \quad B \longrightarrow Y;$$

$$k_2 = 10^{15} e^{\left(-\frac{2000}{T}\right)}$$

$$\int_{\mathbf{Sol.}} r_1 = k_1[\mathbf{A}]$$

$$r_2 = k_2[B]$$

Since [A] = [B],
$$r_1 = r_2$$
 when $k_1 = k_2$

Thus,
$$10^{16} e^{\left(-\frac{3000}{T}\right)} = 10^{15} e^{\left(-\frac{2000}{T}\right)}$$

or
$$16 - \frac{3000}{T \times 2.303} = 15 - \frac{2000}{T \times 2.303}$$

$$1 = \frac{1000}{T \times 2.303}$$
 or $T = \frac{1000}{1 \times 2.303} = 434.22 \text{ K}$

EXAMPLE 4.48

The Arrhenius equation for the rate constant of decomposition of methyl nitrite and ethyl nitrite are

$$k_{\rm J}({\rm s}^{-1}) = 10^{13} \exp\left(\frac{-152300 \text{ J mol}^{-1}}{RT}\right)$$

and
$$k_2(s^{-1}) = 10^{14} \exp\left(\frac{-157700 \text{ J mol}^{-1}}{RT}\right)$$

respectively. Find the temperature at which the rate constants are equal.

Sol. At temperature TK, rate constants are equal, hence

$$10^{13} \exp\left(\frac{-152300 \text{ J mol}^{-1}}{RT}\right) = 10^{14} \left(\frac{-157700 \text{ J mol}^{-1}}{RT}\right)$$

$$\exp\left(\frac{157700 - 152300}{RT}\right) = 10$$

or
$$\log_{e} \exp\left(\frac{157700 - 152300}{RT}\right) = \log_{e} 10$$

= 2.303 $\log_{10} 10$

or
$$\frac{157700 - 152300}{8.314T} = 2.303$$

Thus,
$$T = 282 \text{ K}$$

EXAMPLE 4.49

The activation energy of the reaction: $A + B \longrightarrow Products$ is 105.73 kJ mol-1. At 40°C, the products are formed at the rate of 0.133 mol L⁻¹ min⁻¹. What will be the rate of formation of products at 80°C?

Sol. Let the rate law be defined as

At
$$T_1$$
: $r_1 = k_1[A]^x[B]^y$

At
$$T_2$$
: $r_2 = k_2[A]^x[B]^y$

$$\Rightarrow r_2 = r_1 \left(\frac{k_2}{k_1} \right)$$

Using Arrhenius equation, find k at 40° C.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Rightarrow \log \frac{k_2}{k_1} = \frac{105.73 \times 10^3}{2.303 \times 8.31} \left(\frac{40}{313 \times 353} \right)$$

$$\Rightarrow \log \frac{k_2}{k_1} = 2.0$$

$$\Rightarrow \frac{k_2}{k_1} = 100$$

$$\Rightarrow r_2 = 0.133 \times 100 = 13.3 \text{ mol L}^{-1} \text{ min}^{-1}$$

EXAMPLE 4.50

For a reversible reaction A \Longrightarrow B, if pre-exponential factor is same for both forward and backward reactions, show that $k_{\rm eq} = e^{-\Delta H/RT}$, where ΔH is the heat of reaction.

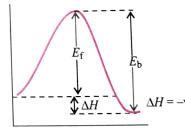
Sol. A $\stackrel{k_f}{\smile}$ B

$$k_{\rm f} = Ae^{-E_{\rm f}/RT}$$

$$k_b = Ae^{-E_b/RT}$$

$$\therefore k_{\rm eq} = \frac{k_{\rm f}}{k_{\rm b}} = e^{(E_{\rm b} - E_{\rm f})/RT}$$

$$=e^{-\Delta H/RT}$$



$$(:: \Delta H = E_{\rm f} - E_{\rm b})$$

EXAMPLE 4.51

Two reactions: $X \longrightarrow Products$ and $Y \longrightarrow Products$ have rate constants k_1 and k_2 at temperature T and activation energies E_1 and E_2 , respectively. If $k_1 > k_2$ and $E_1 < E_2$ (assuming that the Arrhenius factor is same for both the products), then

- **I.** On increasing the temperature, increase in k_2 will be greater than increase in k_1 .
- II. On increasing the temperature, increase in k_1 will be greater than increase in k_2 .

III. At higher temperature, k_1 will be closer to k_2 .

IV. At lower temperature, $k_1 < k_2$

a. I

b. II

c. I, III

d. I, III, IV

Sol.

b. Refer Illustration 4.150.

Since $k_1 \le k_2$ and $E_2 \ge E_1$

From Arrhenius equation $(k = Ae^{-E_a/RT})$, if k_1 is high then E_1 is low. Therefore, with increase in temperature increase in k_1 will be greater than increase in k_2 .

EXAMPLE 4.52

The decomposition of compound A in solution is a first order process with an activation energy of 52.3 kJ mol⁻¹. A 10% solution of A is 10% decomposed in 10 min at 10°C. How much decomposition would be observed with a 20% solution after 20 min at 20°C.

Sol. At 10°C,
$$k_{10^{\circ}} = \frac{2.303}{10} \log \frac{100}{90} = 0.0105 \text{ min}^{-1}$$

$$\log \frac{k_{20}}{k_{10}} = \frac{E_{a}}{2.303R} \left[\frac{T_{2} - T_{1}}{T_{1} T_{2}} \right]$$

$$\log \frac{k_{20}}{0.015} = \frac{52.3 \text{ kJ}}{2.303 \times 8.3 \times 10^{-3}} \log \left[\frac{10}{283 \times 293} \right]$$

$$k_{20} = 0.0224 \text{ min}^{-1}$$

At 20 min,
$$k_{20} = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\frac{0.0224 \times 20}{2.303} = \log \frac{100}{100 - x}$$

$$x = 36.10\%$$

Single Correct Answer Type

Rate of Reaction

Rate experssion and
$$2N_2O_5 \rightarrow 4NO_2 + O_2$$
1. $2N_2O_5 \rightarrow 4NO_2 + O_2$

$$\int_{1}^{2N_2O_5} \frac{2N_2O_5}{dt} = k_1[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k_2[N_2O_5]$$

$$\frac{d[O_2]}{dt} = k_3[N_2O_5]$$

What is the relation between k_1 , k_2 , and k_3 ?

$$(1) k_1 = k_2 = k_3$$

$$(2) \ 2k_1 = k_2 = 4k_3$$

$$\frac{(1)k_1}{(3)} 2k_1 = 4k_2 = k_3$$

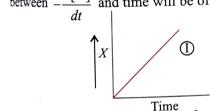
2. For gaseous reaction, the rate is often expressed in terms of dP/dt instead of dc/dt or dn/dt (where c is the concentration and n the number of mol). What is the relation among these three expressions?

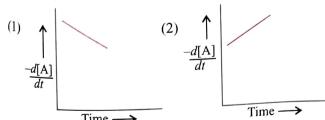
$$(1) \frac{dc}{dt} = \frac{1}{V} \left(\frac{dn}{dt} \right) = \frac{1}{RT} \left(\frac{dP}{dt} \right)$$

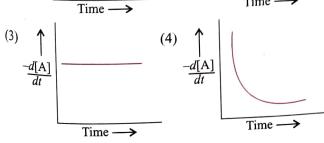
$$(2) \frac{dc}{dt} = \left(\frac{dn}{dt}\right) = \left(\frac{dP}{dt}\right)$$

(3)
$$\frac{dc}{dt} = \left(\frac{dn}{dt}\right) = \frac{V}{RT} \left(\frac{dP}{dt}\right)$$

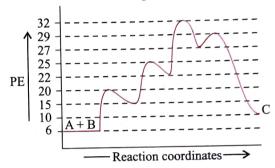
- (4) None of these
- 3. The graph between concentration (X) of the product and time of the reaction $A \rightarrow B$ is of the type I. Hence, graph between $-\frac{d[A]}{dt}$ and time will be of the type:





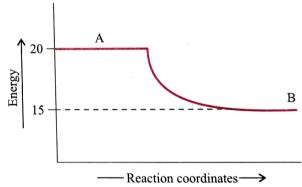


- **4.** For the reaction $X + 3Y \rightarrow Z$, which form of differential rate law is incorrect?
 - (1) dX/dt = dY/3dt
- (2) 3dZ/dt = -dY/dt
- (3) $d\mathbf{Z}/dt = -d\mathbf{X}/dt$
- (4) dX/dt = dZ/dt
- 5. Which of the following will react at the highest rate?
 - (1) 1 mol of A and 1 mol of B in a 1-L vessel
 - (2) 2 mol of A and 2 mol of B in a 2-L vessel
 - (3) 3 mol of A and 3 mol of B in a 3-L vessel
 - (4) All would react at the same rate
- 6. What is ΔH for the reaction $A + B \rightarrow C$ where the mechanism involves several kinetic steps.



- (1) 11 kcal mol⁻¹
- (2) 4 kcal mol⁻¹
- (3) 5 kcal mol⁻¹
- (4) 22 kcal mol⁻¹
- 7. What can you say about the existence of A if the potential energy diagram for the reaction

 $A \rightarrow B$ looks like



- (1) A will exist
- (2) A will not exist
- (3) B will not exist
- (4) A and B are in equilibrium
- 8. For a chemical reaction $2X + Y \longrightarrow Z$, the rate of appearance of Z is 0.05 mol L⁻¹ min⁻¹. The rate of disappearance of X will be
 - (1) $0.05 \text{ mol } L^{-1} \text{ hr}^{-1}$
- (2) $0.05 \text{ mol } L^{-1} \text{ min}^{-1}$
- (3) 0.1 mol L⁻¹ min⁻¹
- (4) 0.25 mol L⁻¹ min⁻¹
- 9. For the reaction: $2HI \rightarrow H_2 + I_2$, the expression -d(HI)/2dtrepresents
 - (1) The rate of formation of HI
 - (2) The rate of disappearance of HI
 - (3) The instantaneous rate of the reaction
 - (4) The average rate of reaction

Physical Chemistry

- 10. The term -dx/dt in the rate expression refers to
 - (1) The concentration of the reactants
 - (2) Increase in the concentration of the reactants
 - (3) The instantaneous rate of the reaction
 - (4) The average rate of the reaction
- 11. If a reaction involves gaseous reactants and products, the units of its rate are
 - (1) atm
- (2) atm-s
- $(3) atm-s^{-1}$
- (4) atm² s²
- 12. Which of the following expressions can be used to describe the instantaneous rate of the reaction?

$$2A + B \rightarrow A_2B$$

- $(1) \frac{dA}{2dt}$
- $(2) \frac{dA}{dt}$
- (3) $\frac{d(A_2B)}{2dt}$ (4) $-\frac{1}{2}\frac{dA}{dt}\frac{dB}{dt}$
- 13. For a reaction $pA + qB \rightarrow Products$, the rate law expression is $r = k[A][B]^m$. Then
 - (1) (p+q) = (1+m)
 - (2) (p+q) > (1+m)
 - (3) (p+q) may or may not be equal to (1+m)
 - (4) (p+q) = (1+m)
- 14. In the formation of sulphur trioxide by the contact process,

$$2SO_3(g) + O_2(g) \Longrightarrow 2SO_3(g)$$

The rate of reaction is expressed as

$$-\frac{d(O_2)}{dt} = 2.5 \times 10^{-4} \,\text{mol L}^{-1} \,\text{s}^{-1}$$

The rate of disappearance of (SO₂) will be

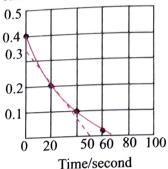
- (1) $5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- $(2) -2.25 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$
- (3) $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
- (4) $50.0 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$
- 15. In a catalytic reaction involving the formation of ammonia by Haber's process $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of appearance of NH₃ was measured as 2.5×10^{-4} mol L⁻¹ s⁻¹. The rate of disappearance or H₂ will be
 - (1) $2.50 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - (2) $1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - (3) $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - (4) $5.00 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$
- 16. The rate constant of forward and backward reactions for certain hypothetical reaction are 1.1×10^{-2} and 1.5×10^{-3} , respectively. The equilibrium constant of the reaction is
 - (1)7.33
- (2) 0.733
- (3)73.3
- (4)733
- 17. The rate of chemical reaction
 - (1) Increases as the reaction proceeds
 - (2) Decreases as the reaction proceeds
 - (3) May increase or decrease during the reaction
 - (4) Remains constant as the reaction proceeds

- 18. At 27°C it was observed in the hydrogenation of a reaction the pressure of H₂(g) decreases from 10 atm to 2 atm in 10 min. Calculate the rate of reaction in M min-1 (Given $R = 0.08 \text{ L atm K}^{-1} \text{ mol}^{-1}$)
 - (1) 0.02

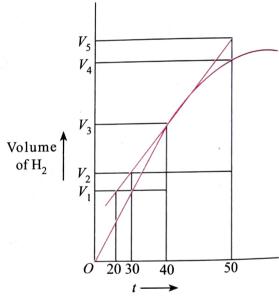
(2) 0.03

(3) 0.04

- (4) 0.05
- 19. A reaction follows the given concentration (C) vs time graph. The rate for this reaction at 20 seconds will be:



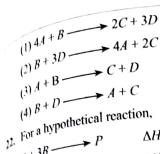
- (1) $8 \times 10^{-2} \,\mathrm{Ms^{-1}}$
- (2) $2 \times 10^{-2} \,\mathrm{Ms^{-1}}$
- $(3) 4 \times 10^{-3} \text{ Ms}^{-1}$
- (4) $7 \times 10^{-3} \text{ Ms}^{-1}$
- 20. A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in figue. On the basis of this mark the correct option.



- (1) Average rate up to 40 s is $\frac{V_3 V_1}{40 20}$
- (2) Average rate up to 40 s is $\frac{V_3 V_2}{40 30}$
- (3) Average rate up to 40 s is $\frac{V_3}{40}$
- (4) Average rate up to 40 s is $\frac{V_3 V_2}{40}$
- 21. The rate of a reaction is expressed in different ways as follows:

$$+\frac{1}{2}\frac{d[C]}{dt} = -\frac{1}{3}\frac{d[D]}{dt} = +\frac{1}{4}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:



$$\Delta H = -2x \text{ kJ/mole of } A$$

For a hypoximize
$$P$$

$$A+3B \longrightarrow P$$

$$M \longrightarrow 2Q+R$$

$$\Delta H = + x \text{ kJ/mole of } M$$

These reactions are carried simultaneously in a reactor such These temperature is not changing. If rate of disappearance that render then rate of formation (in $M \sec^{-1}$) of Q of B is y M sec⁻¹ then rate of formation (in M sec⁻¹) of Q

(1)
$$\frac{2}{3}$$
.

(2)
$$\frac{3}{2}y$$

(3)
$$\frac{4}{2}y$$

(4)
$$\frac{3}{4}y$$

The forward rate constant for the elementary reversible gaseous reaction

$$C_2H_6 \rightleftharpoons 2CH_3 \text{ is } 1.57 \times 10^{-3} \text{ s}^{-1} 100 \text{ K}$$

What is the rate constant for the backward reaction at this temperature of 10^{-4} moles of CH_3 and 10 moles of C_2H_6 are present in a 10 litre vessel at equilibrium.

- (1) $1.57 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$
- (2) $1.57 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
- (3) $1.57 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$
- (4) $1.57 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$

Order and Molecularity of Reaction

- 24. For which of the following reactions, the units of rate constant and rate of reaction are same?
 - (1) First order reaction
 - (2) Second order reaction
 - (3) Third order reaction
 - (4) Zero order reaction
- 25. For a single step reaction $X + 2Y \rightarrow Products$, the molecularity is
 - (1) Zero
- (3)3
- (4) 1
- (2) 226. For a hypothetical reaction $A \rightarrow B$, the rate constant is 0.25 s⁻¹. If the concentration of A is reduced to half, then the value of rate constant is
- (1) 0.25 s^{-1} (2) 0.30 s^{-1} (3) 0.075 s^{-1} (4) 2.25 s^{-1}
- 27. In an acidic medium, the rate of reaction between (BrO $_3^{\odot}$) and Br[©] ions is given by the expression

$$\frac{-d[\text{BrO}_3^{\odot}]}{dt} = k [\text{BrO}_3^{\odot}][\text{Br}^{\odot}][\text{H}^{\oplus}]^2$$

- (1) The rate constant of overall reaction is 4 s^{-1} .
- (2) The rate of reaction is independent of the concentration of acid.

- (3) The change in pH of the solution will not affect the rate.
- (4) Doubling the concentration of H^{\oplus} ions will increase the reaction rate by 4 times.
- 28. For the chemical reaction

$$5\text{Br}^{\Theta} + \text{BrO}_3^{\Theta} + 6\text{H}^{\oplus} \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$$

Rate =
$$k[Br^{\Theta}][BrO_3^{\Theta}][H^{\Theta}]^2$$

The molecularity and order of reaction with respect to $[Br^{\ominus}]$ is

- (1) 5, 1
- (2)1,5
- (3) 1, 1
- 29. For the chemical reaction $I^{\odot} + OCI^{\odot} \rightarrow CI^{\odot} + OI^{\odot}$

Rate =
$$\frac{k[OCl^{\odot}][I^{\odot}]}{[OH]}$$

The order and molecularity of the reaction is

- (1) 1, 2
- (2) 2, 1
- (3) 2, 2
- (4)3,2
- 30. In Q. 29, the molecularity and order with respect to [OH]
 - (1) 0, 1
- (2) 0, -1
- (3)1,0
- (4) -1, 0
- 31. The rate of certain hypothetical reaction

$$A + B + C \rightarrow Products$$
, is given by

$$r = -\frac{dA}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$$

The order of a reaction is given by

- (1) 1
- (2) 1/2
- (3)2
- (4) 13/12
- 32. When ethyl acetate was hydrolyzed in the presence of 0.1 M HCl, the constant was found to be 5.40×10^{-5} s⁻¹. But when 0.1 M H₂SO₄ was used for hydrolysis, the rate constant was found to be 6.20×10^{-5} s⁻¹. From these we can say that
 - (1) H₂SO₄ is stronger than HCl.
 - (2) H₂SO₄ and HCI are both of the same strength.
 - (3) H₂SO₄ is weaker than HCl.
 - (4) The data is insufficient to compare the strength of HCl and H_2SO_4 .
 - 33. The specific rate constant of a first order reaction depends on the
 - (1) Concentration of the reactant
 - (2) Concentration of the product
 - (3) Time
 - (4) Temperature
- 34. The rate constant of a reaction depends on
 - (1) Temperature
- (2) Mass
- (3) Weight
- (4) Time
- 35. The second order rate constant is usually expressed as
 - (1) Mol L s^{-1}
- (2) Mol⁻¹ L⁻¹ s⁻¹
- (3) Mol L^{-1} s⁻¹
- (4) Mol⁻¹ L s⁻¹
- 36. The rate of reaction $A + B \rightarrow Products$ is given by the equation r = k[A][B]. If B is taken in large excess, the order of the reaction would be
 - (1) 2

(2) 1

(3)0

(4) Unpredictable

- 37. The units of rate constant and rate of a reaction are identical
 - (1) zero-order reaction
- (2) first-order reaction
- (3) second-order reaction
- (4) third-order reaction
- 38. The rate law for a reaction between A and B is given by rate = $k [A]^n [B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction becomes

 - (1) $2^{1/(m+n)}$ (2) m+n
- (3) m n
- (4) 2^{n-m}
- **39.** For the chemical reaction $X \longrightarrow Y$, it is found that the rate of reaction increases by 2.25 times when the concentration of X is increased by 1.5 times, what is the order w.r.t. X?
- (2) 1
- (3) 2
- **40.** Consider a reaction $aG + bH \longrightarrow Products$. When concentration of both the reactants G and H is doubled, the rate increases eight times. However, when the concentration of G is doubled, keeping the concentration of H fixed, the rate is doubled. The overall order of reaction is
 - (1)0
- (2) 1
- (3) 2
- (4) 3
- **41.** For a hypothetical reaction $A \rightarrow B$, it is found that the rate constant = x s⁻¹. By what factor the rate is increased if the initial concentration of A is tripled?
 - (1) 1
- (2) 2
- (3)3
- (4)4
- **42.** For a reaction: $nA \longrightarrow Product$, if the rate constant and the rate of reactions are equal, what is the order of the reaction?
 - (1)0
- (2) 1
- (3) 2
- (4) 3
- 43. Analyze the generalized rate data:

 $RX + M^{\odot} \longrightarrow Product$

Experiment	[RX]	[M [⊙]]	Rate
	Substrate	Attacking	
	×	species	
I	0.10 M	0.10 M	1.2×10^{-4}
II	0.20 M	0.10 M	2.4×10^{-4}
III	0.10 M	0.20 M	2.4×10^{-4}
IV	0.20 M	0.20 M	4.8×10^{-4}

The value of rate constant for the given experiment data is

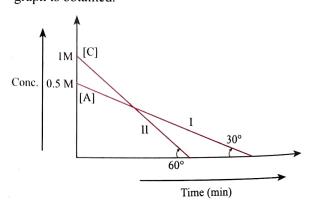
- (1) 1.2×10^{-2}
- (2) 1.2×10^{-4}
- $(3) 1.2 \times 10^{-3}$
- $(4) 2.4 \times 10^{-2}$
- 44. Refer to Q.43 For the reaction under consideration, 3° alkyl has been found to be the most favourable alkyl group. Which of the following attacking species (M^{\odot}) will give the best yield in the reaction?
 - (1) (CH₂)₂CH—O[⊙]
- $(2) (CH_3)_3 C O^{\odot}$

- (4) CH₂CH₂O[⊙]
- 45. For rate constant is numerically the same for three reactions of first, second and third order respectively. Which of the following is correct?
 - (1) If [A] > 1, then $r_3 > r_2 > r_1$
 - (2) If [A] < 1, then $r_1 > r_2 > r_3$

- (3) If [A] = 1, then $r_1 = r_2 = r_3$
- (4) All of the above
- 46. Which of the following statements is not correct about order of a reaction?
 - (1) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.
 - (2) Order of a reaction is experimentally determined quantity
 - (3) The order of a reaction is always equal to the sumof the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction
 - (4) The order of a reaction can be a fractional number
- 47. Trimolecular reactions are uncommon because
 - (1) The probability of three molecules colliding at an instant is low
 - (2) The probability of many molecules colliding at an instant is high
 - (3) The probability of three molecules colliding at an instant is zero
 - (4) The probability of three molecules colliding at an instant is high
- **48.** Which of the following statements is incorrect?
 - (1) A second order reaction must be a bimolecular elementary reaction
 - (2) A bimolecular elementary reaction must be a second order reaction
 - (3) Zero order reaction must be a complex reaction
 - (4) First order reaction may be complex or elementary reaction.
- **49.** Reaction $A \rightarrow B$ follows second order kinetics. Doubling the concentration of A will incraese the rate of formation of B by a factor of:
 - (1) 1/4
- (2) 1/2

(3)2

- (4) 4
- **50.** For the two reactions I: $A \rightarrow B$; II: $C \rightarrow D$ following graph is obtained.



Which of the following is true:

(1) If [B] = [A] then at that time [D] = 0.75

(2) If [C] = [A] then at that time [B] > [D]

(3) $(t_{100\%})_{\text{Reaction I}} = (t_{100\%})_{\text{Reaction II}}$

(3)
$$(t_{100\%})^{T_{Reaction 1}}$$

(4) $[A] = [C]$ at $t = \frac{\sqrt{3}}{2}$ min.

Mechanism of Reaction

The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an superiory process. In an experience, elementary process. In an experiment involving this reaction, the initial partial pressure of A and B are $p_A = 0.60$ atm and $p_B = 0.80$ atm, respectively. When = 0.20 atm, the rate of reaction relative to the initial

$$\frac{\text{rate is}}{(1) \, 1/6} \qquad (2) \, 1/12$$

52. In the decomposition of N₂O₅(g),

$$2N_{1}O_{5}(g) \xrightarrow{k_{008}} 4NO_{2}(g) + O_{2}(g),$$

the observed rate law is given by

$$\frac{d[O_2]}{dt} = k_{\text{obs}}[N_2O_5].$$

Which of the following proposed mechanics is consistent with the rate law?

(1)
$$N_2O_5(g) \xrightarrow{k} N_2O_3(g) + O_2(g)$$

(2)
$$N_2O_5(g) \xrightarrow{k_2} NO_2(g) + NO_3(g)$$

(3)
$$NO_2(g) + NO_3(g) \xrightarrow{k_1} NO(g) + NO_2(g) + O_2(g)$$

(4)
$$NO_3(g) + NO(g) \xrightarrow{k_2} 2NO_2(g)$$

53. Consider the reaction mechanism:

$$A_2 \xrightarrow{k_{eq}} 2A \text{ (fast)}$$
 (where A is the intermediate.)
 $A+B \xrightarrow{k_1} P \text{ (slow)}$

The rate law for the reaction is

(1)
$$k_1[A][B]$$

(2)
$$k_1 k^{1/2} [A_2]^{1/2} [B]$$

(3)
$$k_1 k^{1/2}$$
[A] [B]

(4)
$$k_1 k^{1/2} [A]^2 [B]$$

54. In the formation of HBr from H₂ and Br₂, following mechanism is observed:

(Equilibrium step)

II.
$$H_2 + Br \cdot \longrightarrow HBr + H \cdot$$

(Slow step)

III.
$$H^{\bullet} + Br_2 \longrightarrow HBr + H^{\bullet}$$

(Fast step)

The rate law for the above reaction is

(1)
$$r = k [H_2] [Br_2]$$

(2)
$$r = k [H_2][Br_2]^{1/2}$$

(3)
$$r = k [H_2]^{1/2} [Br_2]$$

(1)
$$r = k [H_2] [Br_2]$$
 (2) $r = k [H_2] [Br_2]^{1/2}$ (3) $r = k [H_2]^{1/2} [Br_2]$ (4) $r = k [H_2]^{1/2} [Br]^{1/2}$

55. The forward reaction rate for the nitric oxide-oxygen reaction

 $2NO + O_2 \xrightarrow{\cdot} 2NO_2$ has the rate law as:

Rate =
$$k [NO]^2 [O_2]$$
.

If the mechanism is assumed to be:

$$2NO \stackrel{k_{eq}}{\rightleftharpoons} N_2O_2$$

(rapid equilibration)

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$
 (slow step),

then which of the following is(are) correct?

I. Rate constant =
$$k_{eq} k_2$$

II.
$$[N_2O_2] = k_{eq} [NO]^2$$

III.
$$[N_2O_2] = k_{eq}[NO]$$

IV. Rate constant = k_2

(2) III, IV

(4) None of these

56. Consider a reaction $X + Y \longrightarrow Products$. If the initial concentration of X is increased to four times of its original value, keeping the concentration of Y constant, the rate of reaction increases four-fold. When the concentration of both X and Y becomes four times their original values, the rate of reaction becomes 16 times its original value. The observed rate law is

(1)
$$k [X]^2 [Y]^2$$

(2)
$$k [X]^1 [Y]^2$$

(3)
$$k [X]^1 [Y]^1$$

(4)
$$k [X]^2 [Y]^1$$

57. The rate law for the reaction $O_3 + O \longrightarrow 2O_2$ is rate = $k[O_3][NO]$. Then which is incorrect?

- (1) NO is catalyst.
- (2) O atom is not involved in slow step.
- (3) The slow step is bimolecular.
- (4) None of these

58. The rate of reaction can not be increased by

- (1) Decreasing threshold energy
- (2) Using a positive catalyst
- (3) Increasing activation energy
- (4) Increasing temperature
- 59. The reaction:

$$OCl_{\bigcirc} + I_{\bigcirc} \xrightarrow[\bigcirc]{OH} OI_{\bigcirc} + Cl_{\bigcirc}$$

takes place in the following steps:

i.
$$OCl^{\odot} + H_2O \xrightarrow{k_1} HOCl + OH$$
 (fast)

ii.
$$I^{\odot} + HOC1 \xrightarrow{k_3} HOI + C1^{\odot}$$

iii.
$$\stackrel{\odot}{OH} + HOI \xrightarrow{k_1'} H_2O + OI^{\odot}$$
 (fast)

The rate of consumption of I^{\odot} in the following equation is

$$(1) \frac{k_3 k_1}{k_2} \frac{[\mathrm{OCl}^{\odot}][\mathrm{I}^{\odot}]}{[\mathrm{OH}]^2}$$

(1)
$$\frac{k_3 k_1}{k_2} \frac{[\text{OCl}^{\odot}][\text{I}^{\odot}]}{[\text{OH}]^2}$$
 (2) $\frac{k_1 k_2}{k_3} \frac{[\text{OCl}^{\odot}][\text{I}^{\odot}]}{[\text{OH}]}$

(3)
$$\frac{k_1 k_3}{k_2} \frac{[\text{OCl}^{\odot}][\text{I}^{\odot}]}{[\text{OH}]}$$
 (4) $\frac{k_2 k_3}{k_1} \frac{[\text{OCl}^{\odot}][\text{I}^{\odot}]}{[\text{OH}]}$

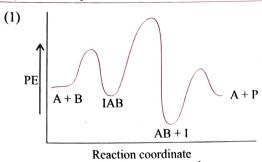
(4)
$$\frac{k_2 k_3}{k_1} \frac{[OC1^{\circ}][1^{\circ}]}{[OH]}$$

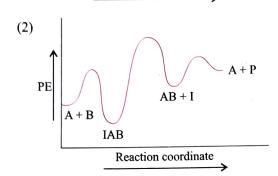
60. The following mechanism has been proposed for the exothermic catalyzed complex reaction:

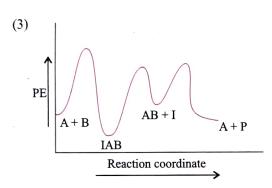
$$A + B \xrightarrow{Fast} IAB \xrightarrow{k_1} AB + I \xrightarrow{k_2} P + A$$

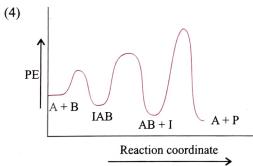
If k_1 is much smaller than k_2 , the most suitable qualitative plot of potential energy (PE) versus reaction coordinates for the above reaction is

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61. The mechanism of the reaction

$$2NO + O_2 \longrightarrow 2NO_2$$
 is

NO + NO
$$\stackrel{k_1}{\longleftarrow}$$
 N₂O₂(fast);

 $N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (slow)

The rate constant of the reaction is

(1)
$$k_{2}$$

$$(2) k_2 k_1 (k_{-1})$$

$$(3) k_2 k_1$$

(2)
$$k_2 k_1 (k_{-1})$$
 (3) $k_2 k_1$ (4) $k_2 \left(\frac{k_1}{k_{-1}}\right)$

62. A following mechanism has been proposed for a reaction:

$$2A + B \longrightarrow D + E$$

$$A + B \longrightarrow C + D$$

(slow)

$$A + C \longrightarrow E$$

(fast)

The rate law expression for the reaction is

(1)
$$r = k[A]^2[B]$$

(2)
$$r = k[A][B]$$

(3)
$$r = k[A]^2$$

$$(4) r = k[A][C]$$

$$A_2 \rightleftharpoons A + A$$

(fast)

$$A + B_2 \rightarrow AB + B$$

$$A + B \rightarrow AB$$

The order of the overall reaction is

- (1) 2
- (2) 1
- (3) 1.5
- (4)0

64. The slowest step of a particular reaction is found to be
$$1/2X_2 + Y_2 \rightarrow XY_2$$
. The order of the reaction is

- (2) 3
- (3) 3.5

65. A reaction
$$A_2 + B_2 \rightarrow 2AB$$
 occurs by the following mechanism:

$$A \rightarrow A + A \dots$$

(slow)

$$A + B_2 \rightarrow AB + B \dots$$

(fast)

$$A + B \rightarrow AB \dots$$

(fast)

- (1) 3/2
- (2) 1
- (3) Zero
- (4)2

66. The chemical reaction
$$2O_3 \rightarrow 3O_2$$
 proceeds as follows:

$$O_3 \rightleftharpoons O_2 + O$$

(fast)

$$O + O_3 \rightarrow 2O_2$$

(slow)

The rate law expression should be

(1)
$$r = k[O_2]^2$$

(2) $r = k[O_3]^2[O_2]^{-1}$

(3)
$$r = k[O_3][O_2]$$

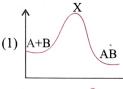
(4) Unpredictable

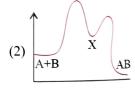
i.
$$A + B \rightarrow X$$

(slow)

ii.
$$X \to AB$$

(fast)







(4) All are correct

68. A plot of logarithm of rate vs logarithm of concentration of the reactant in a first order reaction is straight line whose slope is $tan\theta$, where θ is

 $(1)45^{\circ}$

 $(2) 135^{\circ}$

 $(3) 90^{\circ}$

 $(4) \log k$

69. The rate of radioactive decay of a sample are
$$3 \times 10^8$$
 dps and 3×10^7 dps after time 20 min and 43.03 min respectively. The fraction of radio atom decaying per second is equal to

(2) 1

(3) 0.5

(4) 0.001

Consider the following parallel reactions being given by A 10^2 hours), each path being 6 Constant $t_{1/2} = 1.386 \times 10^2$ hours), each path being first order.



If the distribution of B in the product mixture is 50%, the partial half life of A for conversion into B is

- (1) 231 h
- (2) 131 h
- (3) 115.5 h
- (4) 31 h
- 11. The rate constant for forward reaction $A(g) \rightleftharpoons 2B(g)$ $_{18}^{110}$ 1.5 × 10⁻³ s⁻¹ at 100 K. If 10⁻⁵ moles of A and 100 moles of B are present in a 10-L vessel at equilibrium, then the rate constant for the backward reaction at this temperature
 - .. (1) $1.50 \times 10^{-4} \,\mathrm{L \, mol^{-1} \, s^{-1}}$ (2) $1.50 \times 10^{-11} \,\mathrm{L \, mol^{-1} \, s^{-1}}$ $_{(3)}$ 1.50 × 10⁻¹⁰ L mol⁻¹ s⁻¹ (4) None of these
- 72. The rate law for a reaction between the substance A and B is given by

 $Rate = k[A]^n[B]^m$

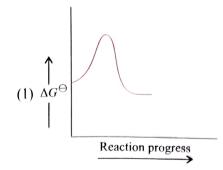
On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier ratio of the reaction will be

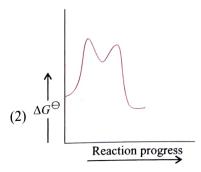
(1)
$$\frac{1}{(2)^{m+n}}$$
 (2) $(m+n)$ (3) $(n-m)$ (4) 2^{n-m}

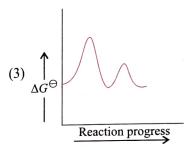
- 73. During the study of kinetics of chemical or nuclear reaction, $t_{1/3}$ can be defined as
 - (1) One-third of the reaction molecules are left.
 - (2) Two-third of the reaction molecules are left.
 - (3) One-third of half of the raction molecules are left.
 - (4) One third of two-thirds of the reaction molecules are left.
- 74. Gadolinium-153, which is used to detect osteoporosis, has a half life of 242 days. After how many days, on an average, a nuclide can be considered absent from patient's system?
 - (1) Infinity
- (2) 350 days
- (3) 242 days
- (4) 4×10^{-3} days
- 75. The rate constant for the hydrolysis of ethyl acetate in the presence of 0.1 N acid (A) was found to be $5.4 \times 10^5 \ s^{-1}$ and for the hydrolysis of ethyl acetate in the presence of 0.1 N acid (B), it was $6.2 \times 10^{-5} \, \mathrm{s}^{-1}$. From these observations, one may conclude that
 - (1) Acids (A) and (B) are both of same strength.
 - (2) Acid (B) is weaker than acid (A).
 - (3) Acid (B) is stronger than acid (A).
 - (4) Data is insufficient.
- 76. For the reaction, $R-X \xrightarrow{Slow} R^{\oplus} + X^{\ominus}$,

$$R^{\oplus} + \stackrel{\odot}{OH} \xrightarrow{Fast} ROH$$

Which type of reaction coordinate diagram represents the above reaction mechanism?







- (4) This is S_N1 reaction where no transition state will be
- 77. The rate constant for zero order reaction is

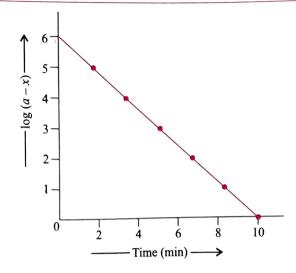
$$(1) k = \frac{c_0}{2t}$$

(2)
$$k = \frac{(c_0 - c_t)}{t}$$

(3)
$$k = \ln\left(\frac{c_0 - c_t}{2t}\right)$$
 (4) $k = \frac{c_0}{c_t}$

$$(4) k = \frac{c_0}{c_k}$$

- 78. Gaseous cyclobutane isomerizes to butadiene in a first order process which has a k value at 153°C of 3.3×10^{-4} s⁻¹. How may minutes would it take for the isomerization to proceed 40% to completion at this temperature?
 - (1) 26 min
- (2) 52 min
- (3) 13 min
- (4) None of these
- 79. The isomerization of cyclopropane to form propene is a first order reaction. At 760 K, 85% of a sample of cyclopropane changes to propene in 79 min. Calculate the value of the rate constant.
 - (1) $3.66 \times 10^{-2} \text{ min}^{-1}$
- (2) $1.04 \times 10^{-2} \,\mathrm{min}^{-1}$
- $(3) 2.42 \text{ min}^{-1}$
- (4) $2.40 \times 10^{-2} \,\mathrm{min^{-1}}$
- 80. The conversion of vinyl allyl ether to pent-4-enol follows first order kinetics. The following plot is obtained for such a reaction:



The rate constant for the reaction is

(1)
$$4.6 \times 10^{-2} \text{ s}^{-1}$$

(2)
$$1.2 \times 10^{-2} \,\mathrm{s}^{-1}$$

(3)
$$2.3 \times 10^{-2} \text{ s}^{-1}$$

(4)
$$8.4 \times 10^{-2} \text{ s}^{-1}$$

81. Calculate the half life of the first-order reaction:

$$C_{\gamma}H_{4}O(g) \longrightarrow CH_{4}(g) + CO(g)$$

The initial pressure of C₂H₄O (g) is 80 mm and the total pressure at the end of 20 min is 120 mm.

82. Aqueous AB, decomposes according to the first order reaction:

$$AB_2(aq) \longrightarrow A(g) + 2B(l)$$

After 20 min the volume of A(g) collected during such a reaction is 20 mL, and that collected after a very long time is 40 mL. The rate constant is:

(1)
$$3.45 \times 10^{-3} \, \text{min}^{-1}$$

(2)
$$3.45 \times 10^{-2} \, \text{min}^{-1}$$

(3)
$$1.435 \times 10^{-2} \, \text{min}^{-1}$$

- 83. The rate constant of a reaction with a virus is 3.3×10^{-4} s⁻¹. Time required for the virus to become 75% inactivated is
 - (1) 35 min
- (2) 70 min
- (3) 105 min (4) 17.5 min
- 84. A Geigger Muller counter is used to study the radioactive process. In the absence of radioactive substance A, it counts 3 disintegration per second (dps). At the start in the presence of A, it records 23 dps; and after 10 min 13 dps,
 - i. What does it count after 20 min?
 - ii. What is the half life of A?
 - (1) 8 dps, 10 min
- (2) 5 dps, 10 min
- (3) 5 dps, 20 min
- (4) 5 dps, 5 min

85.
$$\langle O \rangle$$
 $N_2Cl \xrightarrow{\Delta/Cu} \langle O \rangle$ $Cl + N_2$

Half life is independent of the concentration of A. After $10\,\text{min}$ volume of N_2 gas is $10\,L$ and after complete reaction is 50 L. Hence, the rate constant is

(1)
$$\frac{2.303}{10}$$
 log 5 min⁻¹

(1)
$$\frac{2.303}{10} \log 5 \,\mathrm{min}^{-1}$$
 (2) $\frac{2.303}{10} \log 1.25 \,\mathrm{min}^{-1}$

(3)
$$\frac{2.303}{10} \log 2 \, \text{min}^{-1}$$
 (4) $\frac{2.303}{10} \log 4 \, \text{min}^{-1}$

(4)
$$\frac{2.303}{10} \log 4 \, \text{min}^{-1}$$

86. A \rightarrow Product, $[A]_0 = 2M$. After 10 min reaction is 10%completed. If $\frac{d[A]}{dt} = k[A]$, then $t_{1/2}$ is approximately

(1) 0.693 min

(2) 69.3 min

(3) 66.0 min

(4) 0.0693 min

87.

	$A + B \longrightarrow C$			
10.11	[A]	[B]	[Rate]	
1	1.0	1.0	0.25	
2	2.0	1.0	0.50	
3	1.0	2.0	0.25	

Rate is expressed in mol L⁻¹ min⁻¹.

In the above reaction, the order is

- (1) Zero in A and one in B
- (2) One in A and zero in B
- (3) One in both A and B
- (4) Zero in both A and B
- 88. The rate constant of a reaction is 0.0693 min⁻¹. Starting with 10 mol, the rate of the reaction after 10 min is
 - (1) $0.0693 \text{ mol min}^{-1}$
 - (2) $0.0693 \times 2 \text{ mol min}^{-1}$
 - (3) $0.0693 \times 5 \text{ mol min}^{-1}$
 - (4) $0.0693 \times (5)^2 \text{ mol min}^{-1}$
- 89. The half life of a radioactive element is 20 min. The time interval between the stages of its 33% and 67% decay is
 - (1) 40 min

(2) 20 min

(3) 30 min

(4) 25 min

- 90. 60% of a first order reaction was completed in 60 min. The time taken for reactants to decompose to half of their original amount will be
 - (1) \approx 30 min (2) \approx 45 min (3) \approx 20 min (4) \approx 40 min

- 91. 70% of a first order reaction was completed in 70 min. What is the half life of the reaction?
 - (1) 4.2 min (2) 42 min
- (3) 4.2 hr
- (4) 4.2 s
- 92. 80% of a first order reaction was completed in 70 min. How much it will take for 90% completion of a reaction?
- (1) 114 min (2) 140 min (3) 100 min (4) 200 min
- 93. 90% of a first order reaction was completed in 100 min. How much time it will take for 80% completion of a reaction?
 - (1) 90 min
- (2) 80 min
- (3) 70 min
- (4) 60 min
- 94. 90% of a first order reaction was completed in 100 min. What is the half life of the reaction?
 - (1) 63.3 min (2) 53.3 min (3) 43.3 min (4) 30 min

The hydrolysis of ester in alkaline medium is a

(1) First order reaction with molecularity 1 (1) russ (1) Second order reaction with molecularity > 2

(2) First order reaction with molecularity 2

(3) Find (3) Find (3) Second order reaction with molecularity 1

(4) Second order reaction requires 70 min to change the open A second order reactants from 0.08 M to 0.000 A second to change the A second of reactants from 0.08 M to 0.01 M. How

concerne will it require to become 0.04 M?

(1) 10 min (2) 20 min

(4) 40 min

Select the law that corresponds to data shown for the 97. Select the law that $A + B \rightarrow Product$

following reaction $A + B \rightarrow Products$

llowing 100	[A]	[B]	Initial rate
Exp 1	0.012	0.035	0.1
2	0.024	0.070	0.8
3	0.024	0.035	0.1
4	0.012	0.070	0.8
Rate = $k[I]$	31 ³	(2) Rate	$= k[B]^4$
Maic "L-			

(3) Rate = $k[A][B]^3$

(4) Rate = $k[A]^2[B]^2$

- of If the concentration is measured in mol L-1 and time in minutes, the unit for the rate constant of a third order reaction
 - (1) mol L-1 min-1

(2) $L^2 \text{ mol}^{-2} \text{ min}^{-1}$

(3) L mol⁻¹ min⁻¹

 $(4) \min^{-1}$

- 99. The rate of a reaction increases four-fold when the concentration of reactant is increased 16 times. If the rate of reaction is 4×10^{-6} mol L⁻¹ s⁻¹ when the concentration of the reactant is 4×10^{-4} mol L^{-1} . the rate constant of the reaction will be
 - (1) $2 \times 10^{-4} \text{ mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$ (2) $1 \times 10^{-2} \text{ s}^{-1}$
 - $(3) 2 \times 10^{-4} \text{ mol}^{-1/2} \text{ L}^{1/2} \text{ s}^{-1}$ (4) 25 mol⁻¹ L min⁻¹
- 100. Two substances A and B are present such that $[A_0] = 4[B_0]$ and half life of A is 5 min and that of B is 15 min. If they start decaying at the same time following first order kinetics how much time later will take if the concentration of both of them would be same?
 - (1) 15 min
- (2) 10 min
- (3) 5 min
- (4) 12 min
- 101. A first order reaction: A \longrightarrow Products and a second order reaction: 2R ----- Products both have half time of 20 min when they are carried out taking 4 mol L^{-1} of their respective reactants. The number of mole per litre of A and R remaining unreacted after 60 min from the start of the reaction, respectively, will be
 - (1) 1 and 0.5 M
- (2) 0.5 M and negligible
- (3) 0.5 and 1 M
- (4) 1 and 0.25 M
- 102. The inversion of cane sugar proceeds with half life of 500 min at pH 5 for any concentration of sugar. However, if pH = 6, the half life changes to 50 min. The rate law expression for the sugar inversion can be written as
 - (1) $r = k[sugar]^2[H]^6$
- (2) $r = k[sugar]^{1}[H]^{0}$
- (3) $r = k[\operatorname{sugar}]^0[H^{\oplus}]^6$
- $(4) r = k[\operatorname{sugar}]^0[H^{\oplus}]^1$
- 103. The thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in

- 120 min how long will it take for 90% of the compound to decompose?
- (1) 399 min (2) 410 min (3) 250 min (4) 120 min
- 104. The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_{\rm A}$ = 0.60 and $P_{\rm B}$ = 0.80 atm. When $P_{\rm C}$ = 0.2 atm, the rate of reaction relative to the initial rate is
 - (1) 1/48
- (2) 1/24
- (3) 9/16
- (4) 1/6
- 105. For a first order reaction, $t_{0.75}$ is 1386 s. Therefore, the specific rate constant is
 - (1) 10^{-1} s^{-1}
- (2) 10^{-3} s^{-1}
- $(3)\ 10^{-2}\ s^{-1}$
- (4) $10^{-4} \, \text{s}^{-1}$
- 106. In a first order reaction, the concentration of the reactant decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is
 - (1) 60 min
- (2) 15 min
- $(3) 7.5 \min$
- (4) 30 min
- 107. The rate equation for the reaction $2A + B \rightarrow C$ is found to be: rate = k[A][B]. The correct statement in relation of this reaction is that
 - (1) The value of k is independent of the initial concentration of A and B.
 - (2) $t_{1/2}$ is a constant.
 - (3) The rate of formation of C is twice the rate of disappearance of A.
 - (4) The unit of k must be s^{-1} .
- 108. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mol of A to produce 0.6 mol of B is 1 hr. What is the time taken for the conversion of 0.9 mol of A to product 0.675 mol of B?
 - (1) 1 hr

- (2) 0.5 hr
- (3) 0.25 hr
- (4) 2 hr
- 109. When the rate is determined by the change in concentration of two different reactants, then the kinetic equation may be expressed as
 - (1) $k_2 = \frac{2.303}{(a-b)t} \log \frac{(a-x)b}{(b-x)a}$
 - (2) $k_2 = \frac{2.303}{(a-b)t} \log \frac{(a-x)}{(a+x)}$
 - (3) $k_2 = \frac{2.303}{(a-b)} \log \frac{(a-x)}{(b-x)}$
 - (4) $k_2 = \frac{1}{t} \times \frac{x}{(a-x)}$
- 110. The slope of the line for the graph of $\log k$ versus 1/T for the reaction $N_2O_5 \longrightarrow 2NO_2 + 1/2O_5$ is -5000. Calculate the energy of activation of the reaction (in kJ K^{-1} mol⁻¹).
 - (1)95.7
- (2)9.57

(3)957

(4) None

- 111. The inversion of a sugar follows first order rate equation which can be followed by noting the change in the rotation of the plane of polarization of light in the polarimeter. If r_{∞} , r_t , and r_0 are the rotations at $t = \infty$, t = t, and t = 0, then the first order reaction can be written as
 - (1) $k = \frac{1}{t} \log \frac{r_t r_{\infty}}{r_0 r_{\infty}}$ (2) $k = \frac{1}{t} \ln \frac{r_0 r_{\infty}}{r_t r_{\infty}}$
- - (3) $k = \frac{1}{t} \ln \frac{r_{\infty} r_0}{r_{\infty} r_t}$ (4) $k = \frac{1}{t} \ln \frac{r_{\infty} r_t}{r_{\infty} r_0}$
- 112. For a certain decomposition, the rate is 0.30 M s^{-1} when the concentration of the reactant is 0.20 M. If the reaction is second order, the rate (in M s⁻¹) when concentration is increased three times is
 - (1) 0.30
- (2) 0.90
- (3) 0.60
- (4) 2.70
- 113. For a second order reaction $dx/dt = k(a-x)^2$. Its half life period is

- (1) $\frac{1}{a^{-k}}$ (2) $\frac{0.693}{k}$ (3) $\frac{a}{k}$ (4) $\frac{0.693}{a^k}$
- 114. The dissociation of nitrogen pentaoxide is a first order reaction. In first 24 min, 75% of nitrogen pentaoxide is dissociated. What amount of nitrogen pentaoxide will be left behind after one hour of the start of reaction?
 - (1) Approximately 1%
- (2) Approximately 2%
- (3) Approximately 3%
- (4) None
- 115. In a certain reaction, 10% of the reactant decomposes in one hour, 20% in two hours, 30% in three hours, and so on. The dimension of the velocity constant (rate constant) are
 - $(1) hr^{-1}$

- (2) Mol L^{-1} hr⁻¹
- (3) $L \text{ mol}^{-1} \text{ s}^{-1}$
- (4) Mol s^{-1}
- 116. The decomposition of H_2O_2 can be followed by titration with KMnO₄ and is found to be a first order reaction. The rate constant is 4.5×10^{-2} . In an experiment, the initial titre value was 25 mL. The titre value will be 5 mL after a lapse

 - (1) $4.5 \times 10^{-2} \times 5 \text{ min}$ (2) $\frac{\log_e 5}{4.5 \times 10^{-2}} \text{ min}$
 - (3) $\frac{\log_e 5/4}{4.5 \times 10^{-2}} \text{min}$ (4) None of these
- 117. The half life of decomposition of N_2O_5 is a first order reaction represented by

$$N_2O_5 \longrightarrow N_2O_4 + 1/2O_2$$

After 15 min the volume of O₂ produced is 9 mL and at the end of the reaction 35 mL. The rate constant is equal to

- (1) $\frac{1}{15}\log_e \frac{35}{26}$
- (2) $\frac{1}{15}\log_e \frac{44}{26}$
- (3) $\frac{1}{15} \log_e \frac{35}{36}$
- (4) None of these
- 118. In the reaction $A + B \rightarrow C + D$, the concentration of A and B are equal and the rate of the reaction is rate = k[A][B]. The integrated rate equation for this reaction is

- $(1) \ k = \frac{x}{t(a-x)}$
- (2) $k = \frac{xa}{(a-x)}$
- (3) $k = \frac{1}{t} \cdot \frac{x}{a(x-a)}$ (4) $k = \frac{1}{t} \cdot \frac{x}{a(x-a)}$
- 119. In a second order reaction, 20% of a substance is dissociated in 40 min. The time taken by 80% of its dissociation is (1) 160 min (2) 640 min (3) 200 min (4) 320 min
- 120. $t_{1/2}$ = constant confirms the first order of the reaction as one $a^2t_{1/2} =$ constant confirms that the reaction is of
 - (1) Zero order
- (2) First order
- (3) Second order
- (4) Third order
- 121. For the reaction $2NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$, at 900 K following data are observed.

Initial pressure of NO (atm)	Initial pressure of H ₂ (atm)	Initial rate of pressure decrease (atm min ⁻¹)	
0.150	0.40	0.020	
0.075	0.40	0.005	
0.150	0.20	0.010	

Find out the order of reaction.

- (1) 3
- (2)2
- (3) 1
- (4)0
- 122. The composition of N₂O₅ is a first order reaction represented by: $N_2O_5 \rightarrow N_2O_4 + 1/2O_2$.

After 20 min the volume of O, produced is 10 mL and at the end of the reaction 40 mL. The rate constant is equal to

- (1) $\frac{1}{20} \ln \frac{30}{50}$ (2) $\frac{1}{20} \ln \frac{50}{30}$ (3) $\frac{1}{20} \ln \frac{50}{40}$ (4) $\frac{1}{20} \ln \frac{40}{30}$
- 123. For a hypothetical reaction: $A + B \rightarrow Products$, the rate law is $r = k[A][B]^0$. The order of reaction is
- (2) 1
- (3) 2
- (4)3
- **124.** For hypothetical chemical reaction $A \rightarrow I$, it is found that the reaction is third order in A. What happens to the rate of reaction when the concentration of A is doubled?
 - (1) Rate increases by a factor of 2.
 - (2) Rate decreases by a factor of 3.
 - (3) Rate increases by a factor of 8.
 - (4) Rate remains unaffected.
- 125. What is the order of reaction which has a rate expression rate = $k[A]^{3/2}[B]^{-1}$
 - (1) 3/2

(2) 1/2

(3) Zero

- (4) None of these
- 126. For which of the following represents the expression for three/fourth life of reaction?
 - (1) $\frac{k}{2303} \log 4/3$ (2) $\frac{2.303}{k} \log 3/4$
 - (3) $\frac{2.303}{k} \log 4$
- (4) $\frac{2.303}{k} \log 3$

 $A_2(g) \rightleftharpoons B(g) + 1/2C(g)$ shows B_1^{0} and B_2^{0} in the pressure from 100 mm to 120 A gaseous in the pressure from 100 mm to 120 mm in increase in the pressure of disappearance of A increase $\frac{1}{5}$ min. The rate of disappearance of A_2 is

(1) 4 mm min⁻¹

(2) 8 mm min⁻¹

(3) 16 mm min⁻¹

 $(4) 2 \text{ mm min}^{-1}$

hypothetical reaction $2X + Y \rightarrow M + N$. If the concentration of Y is kept constant but that of X is tripled, the rate of reaction then will be

(1) Increased by 3 times

(2) Increased by 6 times

(3) Increased by 9 times

(4) Unpredictable

[3]. For the reaction $A + B \rightarrow C + D$, doubling the concentration of both the reactants increases the reaction rate by 8 times and doubling the initial concentration of only B simply doubles the reaction rate. The rate law for the reaction is

(1) $r = k[A][B]^2$

(2) r = k[A][B]

(3) $r = k[A]^{1/2}[B]$

(4) $r = k[A]^2[B]$

132. Consider a gaseous reaction, the rate of which is given by k[A][B]. The volume of the reaction vessel containing these gases is suddenly reduced to 1/4th of the initial volume. The rate of the reaction as compared with original rate is

(1) 1/16times

(2) 16 times

(3) 1/8 times

(4) 8 times

133. How will the rate of reaction

 $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ change if the volume of the reaction vessel is halved?

- (1) It will be 1/6th of its initial value.
- (2) It will be 1/4th of its initial value.
- (3) It will be 8 times of its initial value.
- (4) It will be 4 times of its initial value.

134. The half-life period for catalytic decomposition of AB_3 at 50 mm is found to be 4 hr and at 100 mm it is 2.0 hr. The order of reaction is

(1) 3

(3)2

(4) 0

(2) 1135. The hydrolysis of an ester was carried out with 0.1 M $\rm H_2SO_4$ and 0.1 M HCl separately. Which of the following expressions between the rate constants is expected? The rate expression being rate = $k[H^{\oplus}][ester]$

(1) $k_{\text{HCl}} = k_{\text{H}_2\text{SO}_4}$

(2) $k_{\text{HC1}} > k_{\text{H}_2\text{SO}_4}$

(3) $k_{\text{HC1}} < k_{\text{H}_2\text{SO}_4}$

 $(4) k_{\text{H}_2\text{SO}_4} = \tilde{2}k_{\text{HCl}}$

136. In a certain gaseous reaction between A and B, $A + 3B \rightarrow AB_3$. The initial rates are reported as follows:

[A]	[B]	Rate
0.1 M	0.1 M	$0.002~{\rm M}~{\rm s}^{-1}$
0.2 M	0.1 M	$0.002~{\rm M}~{\rm s}^{-1}$
0.3 M	0.2 M	$0.008~{ m M}~{ m s}^{-1}$
0.4 M	0.3 M	$0.018~{ m M}~{ m s}^{-1}$

The rate law is

(1) $r = k[A][B]^3$

(2) $r = k[A]^0[B]^2$

(3) r = k[A][B]

(4) $r = k[A]^0[B]^3$

137. In the presence of acid, the initial concentration, of cane sugar was reduced from 0.2 M to 0.1 in 5 hr and to 0.05 M in 10 hr. The reaction must be of

(1) Zero order

(2) First order

(3) Second order

(4) Fractional order

138. For a reaction, $X(g) \rightarrow Y(g) + Z(g)$. The half-life period is 10 min. In what period of time would the concentration of X be reduced to 10% of the original concentration?

(1) 20 min

(2) 33 min

(3) 15 min

(4) 25 min

139. If a is the initial concentration of reaction, then the half-life period of a reaction of nth order is

 $(1) a^n$

(2) a^{n-1}

(3) a^{1-n}

(4) a^{n+1}

140. When the concentration of a reactant in reaction $A \rightarrow B$ is increased by 8 times but rate increases only 2 times, the order of the reaction would be

(1)2

(2) 1/3

(3)4

(4) 1/2

141. The rate law for the reaction

 $RCl + NaOH(aq) \rightarrow ROH + NaCl$ is given by

Rate = k[RCl]. The rate of the reaction will be

(1) Doubled on doubling the concentration of sodium hydroxide.

(2) Halved on reducing the concentration of alkyl halide to one half.

(3) Decreased on increasing the temperature of the reaction.

(4) Unaffected by increasing the temperature of the reaction.

142. The rate of reaction between A and B increases by a factor of 100, when the concentration with respect to A is increased 10 folds, the order of reaction w.r.t. A is

(1) 10

(2) 1

(3)4

(4) 2

143. For a chemical reaction $A \rightarrow F$, it is found that the rate of reaction doubles when the concentration of A is increased four times. The order in A for this reaction is

(1) 2

(2) 1

(3) 1/2

(4) Zero

144. If the initial concentration of reactants in certain reaction is double, the half-life period of the reaction doubles, the order of a reaction is

(1) Zero

(2) First

(3) Second

(4) Third

145. In a first order reaction, 75% of the reactants disappeared in 1.386 hr. What is the rate constant?

(1) $3.6 \times 10^{-3} \,\mathrm{s}^{-1}$

 $(2) 2.7 \times 10^{-4} \text{ s}^{-1}$

(3) $72 \times 10^{-3} \,\mathrm{s}^{-1}$

(4) $1.8 \times 10^{-3} \,\mathrm{s}^{-1}$

- **146.** A substance "A" decomposes in solution following the first order kinetics. Flask I contains 1 L of 1 M solution of A and flask II contains 100 mL of 0.6 M solution. After 8 hr, the concentration, of A in flask I becomes 0.25 M. What will be the time for concentration of A in flask II to become 0.3 M?
 - (1) 0.4 hr
 - (2) 2.4 hr
 - (3) 4.0 hr
 - (4) Unpredictable as rate constant is not given
- 147. The half-life period of a second order reaction is
 - (1) Proportional to the initial concentration of reactants
 - (2) Independent of the initial concentration of reactants
 - (3) Inversely proportional to the initial concentration of reactants
 - (4) Inversely proportional to the square of initial concentration of reactants
- 148. Diazonium salt decomposes as

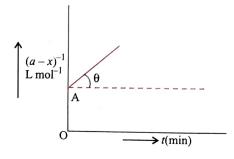
$$C_6H_5N_2^{\oplus}Cl^{\ominus} \rightarrow C_6H_5Cl + N_2$$

At 0° C, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Thus, it is

- (1) A first order reaction
- (2) A second order reaction
- (3) Independent of the initial concentration of reactant
- (4) A zero order reaction.
- **149.** A sample of $_{53}I^{131}$, as I^{\odot} ion, was administered to a patient in a carrier consisting 1.0 mg of stable I^{\odot} ion. After 4.0 days, 60% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable I^{\odot} ion had migrated to the thyroid gland? (Given: $t_{1/2}$ of $I^{131} = 8$ days)
 - (1) 0.65 mg
- (2) 0.75 mg
- (3) 0.85 mg
- (4) 0.95 mg
- **150.** The half life for the viral inactivation if in the beginning 1.5% of the virus is inactivated per minute is (Given: The reaction is of first order)
 - (1) 76 min
- (2) 66 min
- (3) 56 min
- (4) 46 min

Graphical Methods for the Determination of Order of Reaction

151. Following is the graph between $(a - x)^{-1}$ and time t for second order reaction $\theta = \tan^{-1}(0.5)$ OA = 2L mol⁻¹.



Hence, the rate at the start of the reaction is

- (1) 1.25 mol L⁻¹ min⁻¹
- (2) 0.5 mol L⁻¹ min⁻¹
- (3) 0.125 mol L⁻¹ min⁻¹
- (4) 12.5 mol L⁻¹ min⁻¹
- 152. Graph between $\log k$ and 1/T[k is rate constant (s⁻¹) and

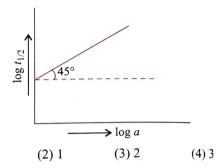
 T is the temperature (K)]

 is a straight line with OX = 5, $\frac{100}{2}$ $\theta = \tan^{-1} (1/2.303)$. Hence $-E_a$ will be
 - (1) 2.303×2 cal
- (2) 2/2.303 cal

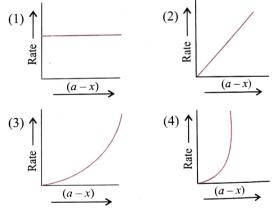
(3) 2 cal

(1) 0

- (4) None
- 153. Following is the graph between $\log T_{50}$ and $\log a$ (a = initial concentration) for a given reaction at 27°C. Hence order is



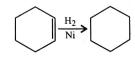
154. Which of the following graphs is for a second order reaction?

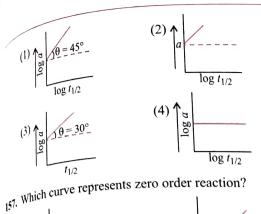


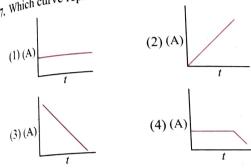
155. The accompanying figure depicts a change in concentration of species A and B for the reaction $A \rightarrow B$, as a function of time. The point of intersection of the two curves represents



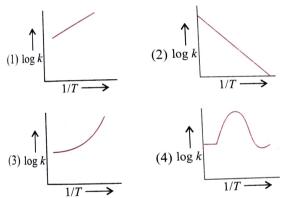
- (1) $t_{1/2}$
- (2) $t_{3/4}$
- (3) $t_{2/3}$
- (4) Data insufficient to predict
- 156. Which of the following is correct graph for the reaction?



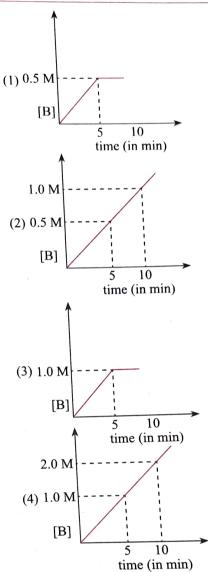




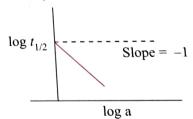
158. A graph plotted between log k versus 1/T for calculating activation energy is shown by



- 159. If a graph is plotted between $\log (a x)$ and t, the slope of the straight line is equal to -0.03. The specific reaction rate will be
 - $(1) 6.9 \times 10^{-2}$
- (2)6.9
- (3) 0.69
- $(4) 6.9 \times 10^{-4}$
- 160. For a zero order reaction, the plot of concentration, vs time is linear with
 - (1) +ve slope and zero intercept
 - (2) -ve slope and zero intercept
 - (3) +ve slope and non-zero intercept
 - (4) -ve slope and non-zero intercept
- 161. The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is first order w.r.t. N₂O₅. Which of the following graphs would yield a straight line?
 - (1) $\log p_{\text{N}_2\text{O}_5}$ vs time with –ve slope
 - (2) $(p_{N_2O_5})^{-1}$ vs time
 - (3) $p_{N_2O_5}$ vs time
 - (4) $\log p_{\text{N}_2\text{O}_5}$ vs time with +ve slope
- $k = 0.1 M \text{ min}^{-1} \rightarrow 2B(g)$. If initial 162. Consider a reaction A(g)concentration of A is 0.5M then select correct graph.



163. A graph between log $t_{1/2}$ and log a (abscissa), a being the initial concentration of A in the reaction. For reaction $A \longrightarrow Product$, the rate law is:



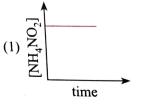
$$(1) \ \frac{-d[A]}{dt} = K$$

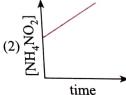
$$(2) \frac{-d[A]}{dt} = K[A]$$

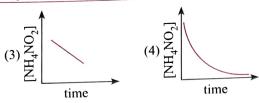
(3)
$$\frac{-d[A]}{dt} = K[A]^2$$
 (4) $\frac{-d[A]}{dt} = K[A]^3$

$$(4) \frac{-d[A]}{dt} = K[A]^3$$

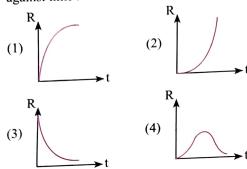
164. Decomposition of NH_4NO_2 (aq) into $N_2(g)$ and $2H_2O(l)$ is first order reaction. Which of the following graph is correct?



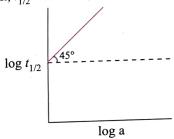




165. If decomposition reaction $A(g) \longrightarrow B(g)$ follows first order kinetics then the graph of rate of formation (R) of B against time t will be:



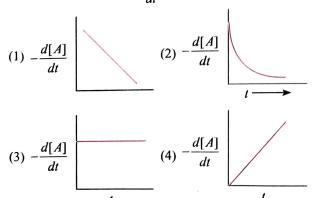
166. What will be the order of reaction for a chemical change having $\log t_{1/2}$ vs $\log a$? (where a = initial concentration of reactant; $t_{1/2} = \text{half-life}$)



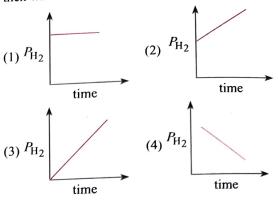
- (1) Zero order
- (2) First order
- (3) Second order
- (4) None of these
- 167. For the reaction $A \longrightarrow B$, for which graph between half-life $(t_{1/2})$ and initial concentration (a) of the reactant is as given below



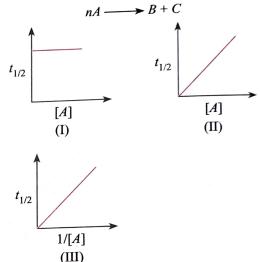
Hence graph between $-\frac{d[A]}{dt}$ and time will be:



168. Decomposition of HI (g) on Gold surface is zero order reaction. Initially few moles of H₂ are present in container then which of the following graph is correct?

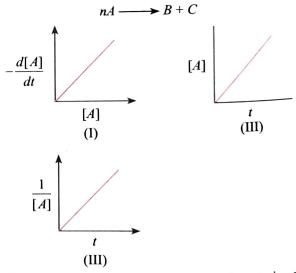


169. Consider the plots, given below, for the types of reaction



These plots respectively correspond to the reaction orders:

- (1) 0, 1, 2
- (2) 1, 2, 0
- (3) 1, 0, 2
- (4) None of these
- 170. Consider the plots for the types of reaction



These plots respectively correspond to the reaction orders:

- (1) 0, 2, 1
- (2) 0, 1, 2
- (3) 1, 1, 2
- (4) 1, 0, 2

11. For a zero order reaction, the plot of conc. (a - x) vs time is linear with is linear with

- (1) +ve slope and zero intercept
- (2) -ve slope and zero intercept
- (3) +ve slope and non-zero intercept
- (4) -ve slope and non-zero intercept

(as Phase, Parallel, and Consecutive Reactions 172. For a homogeneous gaseous reaction $A \longrightarrow 3B$, if pressure after time t was P_T and after completion of pressure was P_{∞} then select correct relation

(1)
$$k = \frac{1}{t} \ln \left(\frac{P_{\infty}}{3(P_{\infty} - P_T)} \right)$$

$$(2) k = \frac{1}{t} \ln \left(\frac{2P_{\infty}}{(P_{\infty} - P_T)} \right)$$

(3)
$$k = \frac{1}{t} \ln \left(\frac{P_{\infty}}{2P_{\infty} - P_T} \right)$$

$$(4) k = \frac{1}{t} \ln \left(\frac{2P_{\infty}}{(P_{\infty} - P_T)} \right)$$

173. For the first order homogeneous gaseous reaction, $A \longrightarrow 2B + C$ then initial pressure was P_i , while total pressure after time 't' was P_t . The right expression for the rate constants k in terms of P_i , P_i and t is:

(1)
$$k = \frac{2.303}{t} \log \left(\frac{2P_i}{3P_i - P_t} \right)$$

(2)
$$k = \frac{2.303}{t} \log \left(\frac{2P_i}{2P_t - P_i} \right)$$

$$(3) k = \frac{2.303}{t} \log \left(\frac{P_i}{P_i - P_t} \right)$$

(4) None of these

174. For a particular reaction with initial conc. of the reactants as a_1 and a_2 , the half-life period are t_1 and t_2 respectively. The order of the reaction (n) is given by:

(1)
$$n = 1 + \frac{\log(t_2/t_1)}{\log(a_2/a_1)}$$
 (2) $n = \frac{\log(t_1/t_2)}{\log(a_2/a_1)}$

(3)
$$n = 1 + \frac{\log (t_1/t_2)}{\log (a_2/a_1)}$$
 (4) None of these

175. The value of $\frac{t_{0.875}}{t_{0.875}}$ for n^{th} order reaction is

(1)
$$2^{(2n-2)}$$

(2)
$$2^{(2n-2)-1}$$

$$(3) \ \frac{8^{n-1}-1}{2^{n-1}-1}$$

(4) None of these

176. A decomposes as:

$$A(g) \xrightarrow{k_1 = 2 \times 10^{-3} \text{ s}^{-1}} 2B(g)$$

$$k_2 = 1 \times 10^{-3} \text{ s}^{-1} \nearrow C(g)$$

The rate of appearance of B, taking 2 M concentration of A, is equal to:

- (1) $2 \times 10^{-3} M \text{ s}^{-1}$
- (2) $4 \times 10^{-3} M \text{ s}^{-1}$
- (3) $8 \times 10^{-3} M \text{ s}^{-1}$
- (4) None of these

177. The reaction $A(g) \longrightarrow B(g) + 2C(g)$ is a first order reaction with rate constant $2.772 \times 10^{-3} \text{ s}^{-1}$. Starting with 0.1 mole of A in 2 litre vessel, find the concentration of Aafter 250 sec when the reaction is allowed to take place at constant pressure and at 300 K?

- (1) 0.0125 M
- (2) 0.025 M
- (3) 0.05 M
- (4) None of these
- 178. $A(aq) \longrightarrow B(aq) + C(aq)$ is a first order reaction.

Time

Moles of reagent

 n_1 n_2

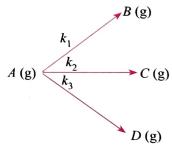
Reaction progress is measured with the help of titration of reagent 'R'. If all A, B and C react with reagent and have

'n' factors [n factor; eq. mass = $\frac{\text{mol. mass}}{n}$] in the ratio of 1:2:3 with the reagent. The k in terms of t, n_1 and n_2 is:

(1)
$$k = \frac{1}{t} \ln \left(\frac{n_2}{n_2 - n_1} \right)$$
 (2) $k = \frac{1}{t} \ln \left(\frac{2n_2}{n_2 - n_1} \right)$

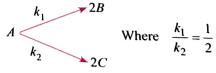
(3)
$$k = \frac{1}{t} \ln \left(\frac{4n_2}{n_2 - n_1} \right)$$
 (4) $k = \frac{1}{t} \ln \left(\frac{4n_2}{5(n_2 - n_1)} \right)$

179. A gaseous compound A reacts by three independent first order processes (as shown infigure) with rate constant 2×10^{-3} , 3×10^{-3} and 1.93×10^{-3} sec⁻¹ for products B, C and D respectively. If initially pure A was taken in a closed container with P = 8 atm, then the partial pressure of B (in atm) after 100 sec from starting the experiment is:



- (1) 0.288
- (2) 0.577
- (3) 1.154
- (4) None of these

180. For given hypothetical elementry parallel reaction,



Initially only 2 moles of A are present. The total no. of moles of A, B and C at the end of 75% reaction are:

(1) 2

(2) 3

(3)4

(4) 3.5

181. A compound A dissociates by two parallel first order paths at certain temperature

$$A (g) \xrightarrow{k_1 \text{ (min}^{-1})} 2B (g) \qquad k_1 = 6.93 \times 10^{-3} \text{ min}^{-1}$$

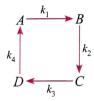
$$A (g) \xrightarrow{k_2 \text{ (min}^{-1})} C (g) \qquad k_2 = 6.93 \times 10^{-3} \text{ min}^{-1}$$

The reaction is started with 1 mole of pure 'A' in 1 litre closed container with initial pressure 2 atm. What is the pressure (in atm) developed in container after 50 minutes from start of experiment?

- (1) 1.25
- (2) 0.75
- (3) 1.50
- **182.** The reaction *cis-X* $\xrightarrow{k_f}$ trans-X is order in both

direction. At 25°C, the equilibrium constant is 0.10 and the rate constant $k_c = 3 \times 10^{-4} \text{ s}^{-1}$. In an experiment starting with the pure cis-form, how long would it take for half of the equilibrium amount of the trans-isomer to be formed?

- (1) 150 sec
- (2) 200 sec
- (3) 240 sec
- (4) 210 sec
- 183. Consider the elementry reaction sequence shown in figure. Which of the following equations are correct?



(1)
$$\frac{d[A]}{dt} = -k_1[A] + k_4[D]$$

(2)
$$\frac{d[C]}{dt} = k_1[B] - k_3[C]$$

(3)
$$\frac{d[D]}{dt} = -k_4[D] + k_3[D]$$

- (4) Can't be predicted
- 184. For the consecutive unimolecular-type first order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component A, (C_{\perp}) at any time t is given by

(1)
$$C_A = C_{A_0} e^{(k_1 + k_2)t}$$
 (2) $C_A = C_{A_0} e^{-(k_1 + k_2)t}$

(2)
$$C_A = C_{A_0} e^{-(k_1 + k_2)}$$

(3)
$$C_A = C_{A_0} e^{-k_1 t}$$
 (4) $C_A = C_{A_0} e^{k_1 t}$

$$(4) \ C_A = C_{A_0} e^{k_1}$$

185. For the consecutive unimolecular-type first-order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component R, (C_R) at any time t is given by:

$$C_R = C_{A_0} K_1 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)} \right]$$

if
$$C_A = C_{A_0}$$
, $C_R = C_{R_0} = 0$ at $t = 0$

The time at which the maximum concentration of R occurs

(1)
$$t_{\text{max}} = \frac{k_2 - k_1}{\ln(k_2 / k_1)}$$
 (2) $t_{\text{max}} = \frac{\ln(k_2 / k_1)}{k_2 - k_1}$

(2)
$$t_{\text{max}} = \frac{\ln (k_2 / k_1)}{k_2 - k_1}$$

(3)
$$t_{\text{max}} = \frac{e^{k_2/k_1}}{k_2 - k_1}$$
 (4) $t_{\text{max}} = \frac{e^{k_2 - k_1}}{k_2 - k_1}$

$$(4) t_{\text{max}} = \frac{e^{k_2 - k_1}}{k_2 - k_1}$$

Energy of Activation, Effect of Temperature and Catalyst

- 186. The half time of a first order reaction is 6.93×10^{-3} min at 27°C. At this temperature, 10⁻⁸ % of the reactant molecules are able to cross-over the energy barrier. The pre-exponential factor A in the Arrhenius equation is equal to
 - (1) $10^4 \,\mathrm{min^{-1}}$ (2) $10^8 \,\mathrm{min^{-1}}$ (3) $10^{10} \,\mathrm{min^{-1}}$ (4) $10^{12} \,\mathrm{min^{-1}}$
- 187. Consider the following reaction at 300 K:

 $A \longrightarrow B$ (uncatalyzed reaction)

 $A \longrightarrow B$ (catalyzed reaction)

The activation energy is lowered by 8.314 kJ mol⁻¹ for the catalyzed reaction. The rate of this reaction is

- (1) 15 times (2) 38 times (3) 22 times (4) 28 times

188. For the given reaction:

$$H_2 + I_2 \longrightarrow 2HI$$

Given:	$T(\mathbf{K})$	1/T (K ⁻¹)	$\log k$	
	769	1.3×10^{-3}	2.9	
	67	1.5×10^{-3}	1.1	

The activation energy will be

- (1) 41.4 kcal mol⁻¹
- (2) 40 kcal mol⁻¹
- (3) -41.4 kcal mol⁻¹
- (4) -40 kcal mol⁻¹
- **189.** In the Arrhenius equation: $k = A \exp(-E_a/RT)$, the rate constant
 - (1) Decreases with increasing activation energy and increases with temperature.
 - (2) Increases with activation energy and temperature.
 - (3) Decreases with activation energy and temperature.
 - (4) Increases with activation energy and decreasing temperature.
- 190. According to the Arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of a chemical reaction ($\log k$) against
 - (1) T
- $(2) \log T$
- (3) 1/T
- (4) $\log 1/T$
- 191. Find out the percentage of the reactant molecules crossing over the energy barrier at 325 K.

Given: $\Delta H_{325 \text{ K}} = 0.12 \text{ kcal};$

$$E_{a(b)} = 0.02 \text{ kcal}$$

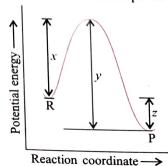
- (1) 80.65%
- (2) 70.65%
- (3) 60.65%
- (4) 50.65%
- 192. In the presence of a catalyst, the rate of a reaction grows to the extent of 105 times at 298 K. Hence, the catalyst must have lowered $E_{\rm a}$ by

- (2) 20 kJ mol⁻¹
- (1) 25 kJ mol⁻¹
- (4) 28.5 kJ mol⁻¹
- White (More than one correct answer)
 - (1) Velocity coefficient of the reaction
 - (2) ΔG^{\odot} of the reaction
 - (3) Energy of activation
 - (4) ΔH of the reaction
- (4) The activation energy of a reaction is zero. The rate constant of this reaction
 - (1) Increases with increase of temperature
 - (2) Decreases with an increase of temperature
 - (3) Decreases with decrease of temperature
 - (4) Is nearly independent of temperature
- The rate of a chemical reaction generally increases rapidly even for small temperature rise because of rapid increases
 - (1) Collision frequency
 - (2) Activation energy
 - (3) Fraction of molecules with energies in excess of the activation energy
 - (4) Average kinetic energy of the molecules
- 196. At a certain temperature, the first order rate constant \boldsymbol{k}_1 is found to be smaller than the second order rate constant k_2 . If $E_a(1)$ of the first order reaction is greater than $E_a(2)$ of the second order reaction, then as temperature is raised:
 - (1) k_2 will increase faster than k_1 .
 - (2) k_1 will increase faster than k_2 but will always remain less than k_2 .
 - (3) k_1 will increase faster than k_2 and become equal to k_2 .
 - (4) k_1 will increase faster than k_2 and become greater than
- 197. A \rightarrow B, $\Delta H = -10$ kJ mol $^{-1}$, $E_{\rm a(f)} = 50$ kJ mol $^{-1}$, then $E_{\rm a}$ of $B \rightarrow A$ will be
 - (1) 40 kJ mol-1
- (2) 50 kJ mol⁻¹
- $(3) -50 \text{ kJ mol}^{-1}$
- (4) 60 kJ mol⁻¹
- 198. The rate of a chemical reaction generally increases rapidly even for small temperature increase because of a rapid increase in
 - (1) Collision frequency
 - (2) Fraction of molecules with energies in excess of the activation energy
 - (3) Activation energy
 - (4) Average kinetic energy of molecules
- 199. Rate constant $k = 1.2 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$ and $E_{\rm a} = 2.0 \times 10^2 \text{ kJ mol}^{-1}$. When $T \to \infty$:
 - (1) $A = 2.0 \times 10^2 \text{ kJ mol}^{-1}$
 - (2) $A = 1.2 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$
 - (3) $A = 1.2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$
 - $(4) A = 2.4 \times 10^3 \text{ kJ mol}^{-1} \text{ s}^{-1}$

- 200. The temperature at which the average speed of perfect gas molecules is double than at 17°C is
 - (1) 34°C
- (2) 68°C
- (3) 162°C
- (4) 887°C
- 201. A catalyst lowers the activation energy of a reaction from 20 kJ mol⁻¹ to 10 kJ mol⁻¹. The temperature at which the uncatalyzed reaction will have the same rate as that of the catalyzed at 27°C is
 - (1) -123°C (2) 327°C
- (3) 32.7°C
- $(4) +23^{\circ}C$
- 202. In a reaction carried out at 500 K, 0.001% of the total number of collisions are effective. The energy of activation of the reaction is approximately
 - (1) 15.8 kcal mol⁻¹
- (2) 11.5 kcal mol⁻¹
- (3) 12.8 kcal mol⁻¹
- (4) zero
- 203. If a reaction $A + B \longrightarrow C$ is exothermic to the extent of 30 kJ mol-1 and the forward reaction has an activation energy, 70 kJ mol-1, the activation energy for the reverse reaction is
 - (1) 30 kJ mol^{-1}
- (2) 40 kJ mol⁻¹
- (3) 70 kJ mol^{-1}
- (4) 100 kJ mol⁻¹
- 204. The rate constant, the activation energy, and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \, \text{s}^{-1} \, 104.4 \, \text{kJ mol}^{-1}$, and $6.0 \times 10^{14} \, \text{s}^{-1}$, respectively. The value of the rate constant as $T \to \infty$ is
 - (1) $2.0 \times 10^{18} \text{ s}^{-1}$
- (2) $6.0 \times 10^{14} \text{ s}^{-1}$

(3) ∞

- (4) $3.6 \times 10^{30} \text{ s}^{-1}$
- 205. A catalyst decreases $E_{\rm a}$ from 100 kJ mol⁻¹ to 80 kJ mol⁻¹. At what temperature the rate of reaction in the absence of catalyst at 500 K will be equal to rate reaction in the presence of catalyst?
 - (1) 400 K
- (2) 200 K
- (3) 625 K
- (4) None of these
- 206. Which of the following expressions give the effect of temperature on the rate constant?
 - (1) $\ln A = RT \ln E_a \ln k$ (2) $\ln k = \ln A E_a/RT$
 - (3) $k = AE_a/RT$
- (4) None of these
- **207.** The plot of $\log k$ vs 1/T helps to calculate
 - (1) The energy of activation
 - (2) The rate constant of the reaction
 - (3) The order of the reaction
 - (4) The energy of activations as well as the frequency factor
- **208.** The potential energy diagram for a reaction $R \rightarrow P$ is given below. ΔH^{\odot} of the reaction corresponds to the energy



	4 Physical Chemistry (1) x	(2) y		` '		ow activation e	
	(3) z (4) (x+y)		(4) In a first order reaction, the reaction ideally tak time to be completed.				
209.	The activation energy $A \rightarrow B$ is E_a in the forward of the reverse reaction	for a simple chemical reaction and reaction. The activation energy	217.		on, the rate con of the activat		ed as $k = Ae^{-40000/T}$.
				(1) 40000 0	cal	(2) 88000 c	al
	(1) Is negative of E_a (2) Is always less than E_a	₹ .		(3) 80000 0	cal	(4) 8000 cal	1
	(3) Can be less than or n		218.	A reaction	takes place in	n three steps.	The rate constants
				are k k	and k . The α	verall rate con	stant $k = \frac{k_1 k_3}{k_2}$. If
	(4) Is always double of B	otosynthesis of					
210.	The quantum yield of ph	(2) HCl < HBr		E_1, E_2 , and	E_3 (energy of	activation) are energy of activa	60, 30, and 10 kJ,
	(1) HCl > HBr	(4) None of these		(1) 40	y, the overan c	(2) 30	action is
	(3) HCl = HBr			(3) 400		(4) 60	
211.	The activation energy of depends upon	f reactant molecules in a reaction	219. A reaction rate constant is given by				
	(1) Temperature			$k = 1.2 \times 10$	$e^{\frac{-2500}{RT}} \mathrm{s}^{-1}$. I	t means	
	(2) Nature of the reactan	ts	(1) $\log k$ versus $\log T$ will give a straight line with a slop				
	(3) Collision per unit time			as 25000.			
	(4) Concentration of reac	ctants	(2) $\log k$ versus $\log T$ will give a straight line with a slope as -25000 .				nt line with a slope
212.	The rate constant of a re	eaction is 1.5×10^{-3} at 25°C and					
	2.1×10^{-2} at 60°C. The a	activation energy is				ve a straight li	ne with a slope as
	(1) $\frac{35}{333}R\log_e \frac{2.1\times10^{-2}}{1.5\times10^{-2}}$	$(2) \ \frac{298 \times 333}{35} R \log_e \frac{21}{1.5}$		-25000.			
	(a) 298 × 333	(4) 298×333 Rlog $\frac{2.1}{2.1}$		(4) $\log k$ ve	rsus 1/1 Will g	give a straight l	activation energy
		$(4) \ \frac{298 \times 333}{35} R \log_e \frac{2.1}{1.5}$		of 17 kI per	r mole of A. T	The heat of the	activation energy reaction is 40 kJ.
213.	In the Wilhelmey equ $c_t = c_0 e^{-kt}$. If the initial	ation of a first order reaction all concentration c_0 is increased		Calculate the $B \rightarrow A$.	ne activation	energy for the	e reverse reaction
	m times, then			(1) 60 kJ	(2) 57 kJ	(3) 75 kJ	(4) 90 kJ
	(1) The value of k will in	acrease m times	221.	$k_{34}^{\circ}; k_{35}^{\circ} < 1$, then		
	(2) The value of k will do	ecrease m times		(1) Rate inci	reases with the	e rise in temper	rature
	(3) The value of k will re	main unchanged				se in temperatu	
21.4	(4) None of these True statement is			(3) Rate doe	es not change v	with rise in ten	perature
214.		eases the rate of reaction.		(4) None of	these		
		the reaction, specific reaction rate	222	A catalyst or	nlv		
	remains constant.	the reaction, specific reaction rate			es activation e	nergy	
		increases with rise in temperature		,	s activation en	•	
	whether the reaction	is endothermic or exothermic.		(3) Both (1)		0.7	
	(4) All are correct.				equilibrium		
	(,) , , , , , , , , , , , , , , , , ,						

215. Collision theory is applicable to

(1) First order reactions

216. The wrong statement is

(3) Bimolecular reactions

lead to a chemical change.

independent of concentration or time.

(2) Zero order reactions

(1) All the collisions between reactant molecules do not

(2) A zero order reaction proceeds at a constant rate

(4) Intermolecular reactions

223. The free energy change due to a reaction is zero when

(4) The reactants are completely consumed

224. In a multistep reaction such as $A + B \rightarrow Q \rightarrow C$. The potential

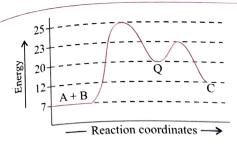
energy diagram is shown below. What is E_a for the reaction

(1) The reactants are initially mixed

(3) The system is at equilibrium

(2) A catalyst is added

 $Q \rightarrow C$?



- (1) 3 kcal mol-1
- (2) 5 kcal mol⁻¹
- (3) 8 kcal mol⁻¹
- (4) 11 kcal mol⁻¹
- 125. ln Q. 224 which statement is true? (1) Reaction $A + B \longrightarrow Q$ is faster.
 - (2) Reaction $Q \longrightarrow C$ is faster.
 - (3) Reaction in (1) and (2) are equal.
 - (4) Unpredictable.
- 126. Given the following two mechanisms, one with catalyst and the other without catalyst.

i.
$$A+B \longrightarrow C$$

(slow)

ii.
$$C+B \longrightarrow F+A$$

(fast)

iii.
$$B+B \longrightarrow F$$

(slow)

Which mechanism uses the catalyst and what is it?

- (1) Step (i), A
- (2) Step (ii), B
- (3) Step (iii), F
- (4) Steps (i) and (ii), C
- 27. The mechanism for the overall reaction is

$$A_2 + B \longrightarrow C$$

$$A_2 \longrightarrow 2A$$

(slow)

$$2A + B \longrightarrow X$$
 (fast)

If a catalyst D changes the mechanism to

$$A_2 + D \longrightarrow A_2D$$

(slow)

$$A_2D \longrightarrow 2A + D$$

(fast)

$$2A + B \longrightarrow C$$

(fast)

Which is the rate expression for the reaction with and without a catalyst?

(1)
$$r = k'[A_2][D], r = k[A_2]$$

(2)
$$r = k[A_2], r = k'[A_2][D]$$

(3)
$$r = k'[A_2D], r = k[A_2][B]$$

(4)
$$r = k[A_2][B], r = k'[A_2D]$$

- 228. Which of the following statement is correct?
 - (1) For reaction $xX \rightarrow yY$

Rate =
$$\frac{1dx}{xdt} = \frac{dy}{dt}$$

- (2) The parameter, rate constant, and specific reaction rate have different meaning.
- (3) For any reaction the value of specific reaction rate is independent of the initial concentration of reactants.
- $(4) E_{a} = E_{R} + E_{Threshold}$
- 229. A chemical reaction occurs as a result of collisions between reacting molecules. Therefore, the reaction rate is given by
 - (1) Total number of collisions occurring in a unit volume per second.
 - (2) Fraction of molecules which possess energy less than the threshold energy.

- (3) Total number of effective collisions.
- (4) None of these
- 230. For producing effective collisions, the colliding molecules must have
 - (1) A certain minimum amount of energy
 - (2) Energy equal to or greater than threshold
 - (3) Proper orientation
 - (4) Threshold energy and proper orientation both
- 231. The rate of reaction increases by the increase of temperature because
 - (1) Collision frequency is increased.
 - (2) Energy products decreases.
 - (3) Fraction of molecules possessing energy $\geq E_{T}$ (threshold energy) increases.
 - (4) Mechanism of a reaction is changed.
- 232. Which of the following explains the increase of the reaction rate by catalyst?
 - (1) Catalyst decreases the rate of backward reaction so that the rate of forward reaction increases.
 - (2) Catalyst provides extra energy to reacting molecules so that they may produce effective collisions.
 - (3) Catalyst provides an alternative path of lower activation energy to the reactants.
 - (4) Catalyst increases the number of collisions between the reacting molecules.
- 233. Burning of coal is represented as $C(s) + O_{\gamma}(g) \rightarrow CO_{\gamma}(g)$. The rate of this reaction is increased by
 - (1) Decrease in the concentration of oxygen
 - (2) Powdering the lumps of coal
 - (3) Decreasing the temperature of coal
 - (4) Providing inert atmosphere
- 234. The rate of a certain reaction increases by 2.3 times when the temperature is raised from 300 K to 310 K. If k is the rate constant at 300 K, then the rate constant at 310 K will be equal to
 - (1) 2k
- (2) k
- (3) 2.3k
- $(4) 3k^2$

235. For the reaction:

$$[Cr(H_2O)_6]^{3+}+[SCN^{\odot}] \rightarrow [Cr(H_2O)_5NCS]^{2+}H_2O$$

The rate law is: $r = k[Cr(H_2O)_6]^{3+}[SCN^{\odot}]$.

The value of k is 2.0×10^{-6} L mol⁻¹ s⁻¹ at 14°C and 2.2×10^{-5} L mol⁻¹ s⁻¹ at 30°C. What is the value of E_a ?

- (1) 26 kcal mol⁻¹
- (2) 2.6 kcal mol⁻¹
- (3) 2600 kcal mol⁻¹
- (4) 260 kcal mol⁻¹
- 236. It is generalized that a 10°C increase in temperature causes the rate of reactions to double. Applied to a reaction at 295 K, what is the value of E_a ?
 - (1) 120 kcal mol⁻¹
- (2) 1200 kcal mol⁻¹
- (3) 1.2 kcal mol⁻¹
- (4) 12 kcal mol⁻¹
- 237. The activation energy for the forward reaction $X \to Y$ is 60 kJ mol⁻¹ and ΔH is -20 kJ mol⁻¹. The activation energy for the reverse reaction is

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(1) 40 kJ mol⁻¹

(2) 60 kJ mol⁻¹

(3) 80 kJ mol⁻¹

(4) 20 kJ mol⁻¹

238. What specific name can be given to the following sequence of steps:

 $Hg + hv \rightarrow Hg^*$

 $Hg^* + H_2 \rightarrow H_2^* + Hg$

(1) Fluorescence

(2) Phosphorescence

(3) Photosensitization

(4) Chemiluminescence

239. In fire flies the flashes are produced due to the slow combustion of a protein luciferin in air and moisture. The phenomenon is known as

(1) Photochemical change

(2) Photocombustion

(3) Chemiluminescence

(4) None of these

240. The activation energy for a hypothetical reaction $A \rightarrow X$ is 12.49 kcal mol-1. If temperature is raised to 305 from 295 K, the reaction rate increased by 0.002 kcal K^{-1} mol $^{-1}$ is almost equal to

(1) 60%

(2) 50%

(3) 100%

(4) Unpredictable

241. The activation energy for most of the reaction is approximately 50 kJ mol-1. The rate for temperature coefficient for such reaction will be

 $(1) \approx 2$

(2) ≈3

(3) < 1

(4) > 4

242. Which of the following theory is not related to the chemical kinetics?

(1) Collision theory

(2) Absolute theory

(3) Absolute reaction rate (4) VSEPR theory

243. Phosphorus undergoes slow combustion and glows in dark. The process is called

(1) Photochemical change (2) Chemiluminescence

(3) Flourescence

(4) Phosphorescence

244. The efficiency of an enzyme in catalyzing a reaction is due to its capacity

(1) To form a strong enzyme-substrate complex.

(2) To decrease the bond energy of all substrate molecules.

(3) To change the shape of the substrate molecule.

(4) To lower the activation energy of the reaction.

245. When KClO₃ is heated, it decomposes into KCl and O₂. If some MnO2 is added, the reaction goes much faster because

(1) MnO_2 decomposes to give O_2 .

(2) MnO₂ provides heat by reacting.

(3) Better contact is provided by MnO₂.

(4) MnO₂ acts as a catalyst.

246. A catalyst

(1) Increases the free energy change in the reaction

(2) Decreases the free energy change in the reaction

(3) Does not increase or decrease the free energy change in the reaction

(4) Can either increase or decrease the free energy change depending on what catalyst we use

247. Mark the correct statement in a reversible reaction

(1) A catalyst catalyzes the forward reaction

(2) A catalyst catalyzes the backward reaction.

(3) A catalyst influences a direct and a reverse reaction to the same extent.

(4) A catalyst increases the rate of forward reaction and decreases the rate of backward reaction.

248. Which of the following statements regarding catalyst is not

(1) A catalyst remains unchanged in composition and quantity at the end of the reaction.

(2) A catalyst can initiate a reaction.

(3) A catalyst does not alter the equilibrium in a reversible reaction.

(4) Catalysts are sometimes very specific in respect of reaction.

249. An example of autocatalytic reaction is

(1) Decomposition of nitroglycerine

(2) Thermal decomposition of KClO₃ and MnO₂ mixture

(3) Breakdown of ¹⁴C₆

(4) Hydrogenation of vegetable oil using nickel catalysts

250. A catalysts is used

(1) Only for increasing the velocity of a reaction

(2) For altering the velocity of a reaction

(3) Only for decreasing the velocity of a reaction

(4) All (1), (2), and (3) are correct

251. The oxidation of oxalic acid by acidified KMnO₄ is an example of autocatalysis. It is due to which of the following?

(1) SO_4^{2-}

(2) MnO_{Λ}^{2-}

(3) Mn^{2+}

(4) K[⊕]

252. For the first order reaction $A \longrightarrow B + C$, carried out at 27°C. If 3.8×10^{-16} % of the reactant molecules exists in the activated state, the $E_{\rm a}$ (activation energy) of the reaction is:

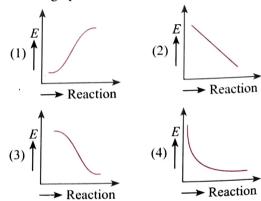
(1) 12 kJ mol

(2) 831.4 kJ mol

(3) 100 kJ mol

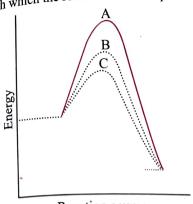
(4) 88.57 kJ mol

253. Which graph shows zero activation energy?



254. A homogeneous catalytic reaction takes place through the three alternative plots A, B and C shown in the given

Which one of the following indicates the relative



Reaction course

$$(1) A > B > C$$

(2)
$$C > B > A$$

$$(3) A > C > B$$

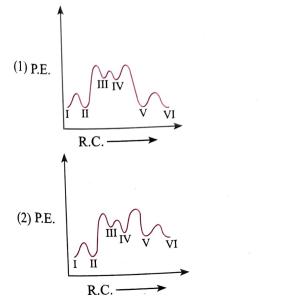
(4)
$$A = B = C$$

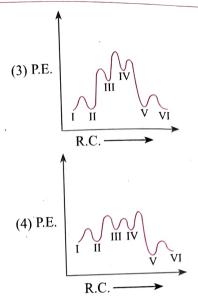
255. The mechanism of esterification in presence of acid catalyst (H₂SO₄) is proposed as follows:

$$(I) \xrightarrow{k_1 \atop H^{\oplus}(fast)} CH_3 \xrightarrow{CO-H} \xrightarrow{+C_2H_5OH} CH_3 \xrightarrow{C-O-H} CH_3 \xrightarrow{(slow)} k_2 \atop -C_2H_5OH} CH_3 \xrightarrow{C-O-H} (III)$$

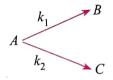
$$\begin{array}{c} \begin{array}{c} & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$$

Which of the following potential energy Vs reaction coordinate diagram is consistent with given mechanism?





256. For first order parallel reactions k_1 and k_2 are 4 and 2 min⁻¹ respectively at 300 K. If the activation energies for the formation of B and C are respectively 30,000 and 38,314 joule/mol respectively, the temperature at which B and C will be obtained in equimolar ratio is:



(1) 757.48 K

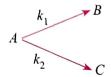
(2) 378.74 K

(3) 600 K

(4) None of these

- 257. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate with same frequency factor, the temperature required is 400 K. What is the activation energy of the reaction, if the catalyst lowers the activation energy barrier by 16 kJ/mol?
 - (1) 100 kJ/mol
- (2) 80 kJ/mol
- (3) 60 kJ mol
- (4) None of these
- **258.** For reaction $A \longrightarrow B$, rate constant $k_1 = A_1 e^{-E_{a_1}/(RT)}$ and for the reaction $X \longrightarrow Y$, the rate constant $k_2 = A_2 e^{-E_{a_2}/(RT)}$. If $A_1 = 10^8$, $A_2 = 10^{10}$ and $E_{a_1} = 600$ cal/mol, $E_{a_2} = 1800$ cal/mol, then the temperature at which $k_1 = k_2$ is (Given: R = 2 cal/K-mol)
 - (1) 1200 K
- (2) $1200 \times 4.606 \text{ K}$
- (3) $\frac{1200}{4.606}$ K (4) $\frac{600}{4.606}$ K

259. Consider the reaction.



The rate constant for two parallel reaction were found to be $10^{-2}~dm^3~mol^{-1}~s^{-1}$ and $4\times10^{-2}~dm^3~mol^{-1}~s^{-1}.$ If the corresponding energies of activation of the parallel

reaction are 100 and 120 kJ/mol respectively, what is the net energy of activation (E_a) of A?

- (1) 100 kJ/mol
- (2) 120 kJ/mol
- (3) 116 kJ/mol
- (4) 220 kJ/mol
- 260. A reaction takes place in various steps. The rate constant for first, second, third and fifth steps are k_1 , k_2 , k_3 and k_5 respectively, the overall rate constant is given by

$$k = \frac{k_2}{k_3} \left(\frac{k_1}{k_5}\right)^{1/2}$$

If activation energy are 40, 60, 50 and 10 kJ/mol respectively, the overall energy of activation (kJ/mol) is:

- $(1)\ 10$
- (2)20

(3)25

(4) None of these

Multiple Correct Answers Type

Rate expression and Rate of Reaction

- 1. In a reaction $2X + Y \longrightarrow X_2Y$, the reactant X will disappear
 - (1) Half the rate as that of disappearance of Y
 - (2) The same rate as that of disappearance of Y
 - (3) Twice the rate as that of appearance of X_2Y
 - (4) Twice the rate as that of disappearance of Y
- 2. In acidic medium, the rate of reaction between BrO₃[©] and Br[⊕] is given by the expression

$$\frac{-d[\text{BrO}_3^{\odot}]}{dt} = k[\text{BrO}_3^{\odot}][\text{Br}^{\odot}][\text{H}^{\oplus}]^2$$

- (1) The rate constant of the reaction depends upon the concentration of H[⊕] ions.
- (2) The rate of reaction is independent of the concentration of the acid added.
- (3) Doubling the concentration of H[⊕] ions will increase the reaction rate by 4 times.
- (4) The change in pH of the solution will affect the rate of reaction.
- 3. For a gaseous reaction: $A(g) \longrightarrow B(g)$, the rate expression may be given as

 - (1) $-\frac{d[A]}{dt} = k[A]^n$ (2) $-\frac{1}{V}\frac{dn_A}{dt} = k[A]^n$
 - (3) $-\frac{1}{RT}\frac{dP_{A}}{dt} = k[A]^{n}$ (4) $-\frac{dP}{dt} = k[P_{A}]^{n}$
- 4. The rate of formation of $C_6H_6 + 3H_2 \xrightarrow{k_1} C_6H_{12}$ for the forward reaction is first order with respect to C₆H₆ and H₂

each. Which one of the options is/are correct?

- (1) $k_{eq} = \frac{k_f}{k_b}$ (2) $k_{eq} = \frac{[C_6 H_{12}]}{[C_6 H_6 || H_2]^3}$
- (3) $r_b = k_b [C_6 H_b] [H_2]$ (4) $r_b = k_b [C_6 H_{12}] [H_2]^{-2}$

- 5. Which of the following statements is/are correct?
 - (1) For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH₃ is 0.001 kg h⁻¹. The rate of conversions of H₂ under the same conditions is 0.0015 kg hr⁻¹.
 - (2) The rate law for the reaction

 $RCI + NaOH(aq) \longrightarrow ROH + NaCI$

is given by, rate = $k_1[RCI]$. The rate of the reaction w_{ijl} be halved on reducing the concentration of alkyl halide to one half.

- (3) The rate of the reaction in part (2) increased on decreasing the temperature of the reaction.
- (4) The rate of chemical change is inversely proportional to the concentration at that instant.
- 6. Select the correct statement(s):
 - (1) The rate of reaction decreases with decrease in temperature
 - (2) The rate of reaction is uniform in zero order reaction
 - (3) The rate of reaction depends upon the surface area of the solid reactants
 - (4) Average and instantaneous rate of reaction defined for micro and marcoscopic time interval respectively.
- 7. Select the correct statement(s):
 - (1) Every substance that appears in the rate law of reaction must be a reactant or product in that reaction
 - (2) If we know the rate law of a reaction; we can deduce its mechanism
 - (3) It the reaction has rate $r = k [A][B]^{3/2}$ then reaction may be elementary
 - (4) A zero order reaction must be a complex reaction
- **8.** Consider a reaction $A + B \rightarrow C$, in which both reactants are in the same phase. The reaction may be
 - (1) Unimolecular elementary reaction
 - (2) Exothermic
 - (3) Heterogeneous
 - (4) Photochemical

Order and Molecularity of a Reaction

- 9. Taking the reaction, $A + 2B \longrightarrow Products$, to be of second order, which of the following is/are the correct rate law expression(s)?

 - $(1) \frac{dx}{dt} = k[A]^2 \qquad (2) \frac{dx}{dt} = k[A][B]^2$

 - (3) $\frac{dx}{dt} = k[A][B]$ (4) $\frac{dx}{dt} = k_1[A] + k_2[B]^2$
- 10. Which of the following statement(s) is/are correct?
 - (1) Zero order reactions are complex reactions.
 - (2) A reaction having first order may be either elementary or complex reaction.

- (3) A reaction having second order reaction must have alecularity = 2. molecularity = 2.
- (4) A reaction with molecularity = 2 must be a second order $\frac{A}{A}$
- Which of the following reaction(s) is/are of the first order?

 11. Which of the decomposition of ammonium pitch. Which of the decomposition of ammonium nitrate in an aqueous (1) The decomposition of ammonium nitrate in an aqueous solution.
 - (2) The inversion of cane sugar in the presence of an acid.
 - (3) The acidic hydrolysis of ethyl acetate.
 - (4) All radioactive decays.
- 12. Which of the following isomerization reactions is/are of the first order?

 - (2) cis-But-2-ene \longrightarrow Trans-but-2-ene
 - (3) Vinyl allyl ether \longrightarrow Pent-4-enal
 - (4) CH₃NC \longrightarrow CH₃CN
- 13. Which of the following is/are examples of unimolecular

$$(1) O_3 \longrightarrow O_2 + O$$

$$(2) \longrightarrow Me$$

$$(3) NO + O_3 \longrightarrow NO_2 + O_2$$

$$(4) O + NO + N_2 \longrightarrow NO_2 + N_2$$

14. Which of the following is/are examples of pseudo unimolecular reactions?

$$(1) CH3CO2C2H5 + H2O \xrightarrow{H^{\oplus}} CH3CO2H + C2H5OH$$

(2)
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$$
(Fructose)

$$(3) \operatorname{CH_3COCl} + \operatorname{H_2O} \longrightarrow \operatorname{CH_3CO_2H} + \operatorname{HCl}$$

$$(4) CH3CO2C2H5 + H2O \xrightarrow{OOH} CH3CO2H + C2H5OH$$

- 15. Which of the following statements is/are correct?
 - (1) The rate of the reaction involving the conversion of ortho-hydrogen to parahydrogen is $-\frac{d[H_2]}{dt} = k[H_2]^{3/2}$.

 (2) The rate of the reaction involving the thermal
 - decomposition of acetaldehyde is $k[CH_3CHO]^{3/2}$.
 - (3) In the formation of phosgene gas from CO and Cl₂, the rate of the reaction is $k[CO][Cl_2]^{1/2}$.
 - (4) In the decomposition of H_2O_2 , the rate of the reaction is $k[H_2O_2].$
- 16. Select the Correct statement
 - (1) Units of rate constant (k') for pseudo unimolecular reaction, when order of reaction is one but molecularity of reaction is two ,represents a second order reaction i.e., L mol $^{-1}$ t $^{-1}$
 - (2) Units of rate constant (k') for pseudo unimolecular reaction when O.R = 1, but molecularity of reaction = 3, represents a third order reaction i.e., $L^2 \text{ mol}^{-2} t^{-1}$.

- (3) Unit of rate constant (k') for pseudo bimolecular reaction, when O.R. = 2, but molecularity = 3, represents a third order reaction i.e., $L^2 \text{ mol}^{-2} t^{-1}$.
- (4) Unit of rate constant (k') for pseudo bimolecular reaction when O.R = 2, but molecularity of reaction = 4, represents a fourth order reaction i.e., L^3 mol⁻³ t^{-1} .

Mechanism of Reaction

17. The rate expression for the reaction:

NH₄CNO \Longrightarrow NH₂CONH₂ can be derived from he mechanism:

i.
$$NH_4CNO \xrightarrow{k_1 \atop k_2} NH_4NCO$$
 (Fast)

ii.
$$NH_4NCO \xrightarrow{k_3} NH_3 + HNCO$$
 (Fast)

iii.
$$NH_3 + HNCO \xrightarrow{k_4} NH_2CONH_2$$
 (Slow)

Which of the following statement(s) is/are correct about the rate expression?

(1)
$$\frac{d_{\text{[urea]}}}{dt} = \frac{k_1 k_3}{k_2} [\text{NH}_4 \text{NCO}]$$

(2)
$$\frac{d_{\text{[urea]}}}{dt} = \frac{k_1 k_3}{k_2 k_4} [\text{NH}_4 \text{NCO}]$$

(3)
$$\frac{d_{\text{[urea]}}}{dt} = k[\text{NH}_4\text{NCO}]$$

(4)
$$\frac{d_{\text{[urea]}}}{dt} = \frac{k_1 \times k_2}{k_3 \times k_4} [\text{NH}_4 \text{NCO}]$$

18.
$$H \xrightarrow{\text{Et}} \text{Cl} + \overset{\ominus}{\text{OH}} \longrightarrow H \xrightarrow{\text{Et}} \text{OH} + \text{OH} \xrightarrow{\text{He}} H$$

Me

Me

I

II

Which of the following statements is/are correct?

- (1) It is unimolecular nucleophilic substitution reaction $S_N 1$ if I or II is formed.
- (2) It is bimolecular nucleophilic substitution reaction S_N2 if I or II is formed.
- (3) It is $S_N 1$ if I and is enantiomer are formed so that the mixture is racemic.
- (4) It is $S_N 2$ if II is formed.

Experimental Determination of Order of Reaction by Various Methods, Half Life and Average Life)

- 19. A reaction is 10% complete in 5 min and 50% complete in 25 min. Which of the following is/are correct?
 - (1) Order of reaction is one.
 - (2) Order of reaction is zero.
 - (3) Reaction will be complete in finite time.
 - (4) Reaction will be complete in infinite time.
- 20. The correct statement(s) are
 - (1) Order of a reaction is an experimental property.

- (2) Order may change with change in experimental conditions.
- (3) Molecularity concerns with mechanism while order concerns with kinetics.
- (4) A reaction taking place by bimolecular collision must always be of second order.
- 21. For zero order reaction which is (are) true?
 - (1) The rate constant is dimensionless.
 - (2) Amount of the reactant remains the same throughout.
 - (3) $t_{1/2} \propto \text{initial concentration of the reactant.}$
 - (4) A plot of concentration of reactant vs time is a straight. line with slope equal to -k.
- 22. In a 1st order reaction, amount of the substance left after n half lives and average life of a 1^{st} order reaction respectively are
 - (1) $\frac{[A_0]}{2^n}$, $\frac{1}{k}$
- (2) $\frac{[A_0]}{n^2}$, 1.44 $t_{1/2}$
- (3) $\frac{[A_0]}{n^{2^n}}$, 1.44 × $t_{1/2}$ (4) $\frac{[A_0]}{n^2}$, $\frac{1}{k}$
- 23. Which of the following relationship(s) are correct for 1st order reaction?
 - (1) $t_{75\%} = 2t_{1/2}$
- $(2) \ t_{87.5\%} = 3t_{1/2}$
- (3) $t_{96.87\%} = 4t_{1/2}$
- $(4) \quad t_{99.9\%} = 9t_{1/2}$
- 24. The bromination of acetone that occurs in acid solution is respresented by

$$\text{CH}_3\text{COCH}_3(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCHBr}_2(\text{aq}) + \text{HBr}(\text{aq})$$
Given:

Exper- iment	Initia	l concentration,	Initial rate Disppearance of Br ₂ , Ms ⁻¹	
	[Br ₂]	[CH ₃ COCH ₃]	[H [⊕]]	
1	0.050	0.30	0.050	5.7×10^{-5}
2	0.10	0.10 0.30		5.7×10^{-5}
3	0.10	0 0.30		1.2×10^{-4}
4	0.050	0.050 0.40		3.1×10^{-4}

Based on the above data, which does not represent rate law are:

(1)
$$\left(\frac{dx}{dt}\right) = k[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^{\oplus}]^2$$

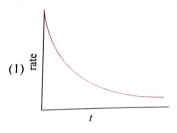
(2)
$$\left(\frac{dx}{dt}\right) = k[CH_3COCH_3][H^{\oplus}]$$

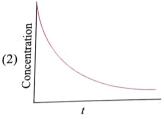
(3)
$$\left(\frac{dx}{dt}\right) = k[CH_3COCH_3][Br_2]$$

(4)
$$\left(\frac{dx}{dt}\right) = k[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^{\oplus}]$$

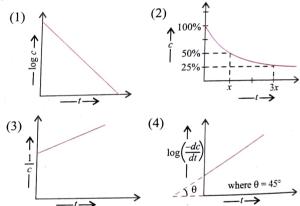
Graphical Method for the Determination of order of $R_{\mbox{\scriptsize eaction}}$

25. Which of the following is/are correct about the first order reaction?





- (3) Half life depends on temperature.
- (4) Rate constant is directly proportional to temperature.
- 26. The correct nature of plot for first order reaction is (are):



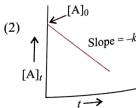
- 27. Which of the following statement(s) are not correct?
 - (1) A plot of $\log k_{\rm p}$ versus 1/T is linear
 - (2) A plot of $\log k_{\rm p}$ versus 1/T is nonlinear.
 - (3) A plot of $\log P$ versus 1/T is linear at constant volume.
 - (4) A plot of P versus 1/V is linear at constant temperature.
- 28. Which of the following graphs represents zero order if

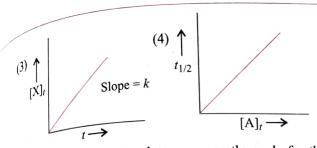
$$A \longrightarrow P$$

$$At t = 0 \Rightarrow [A]_0$$

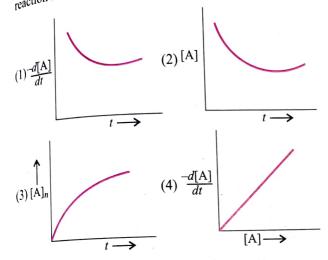
At
$$t = t \Rightarrow [A]_t$$



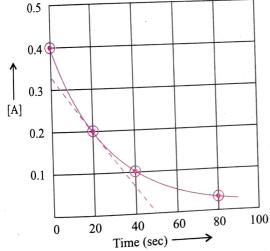




Which of the following plots are correctly made for the reaction $nA \rightleftharpoons (A)_n$ if it obeys first order reaction?



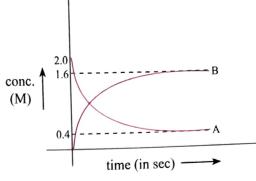
30. A certain reaction A → B follows the given concentration (Molarity)-time graph. Which of the following statements is/are true?



- (1) The reaction is second order with respect to A.
- (2) The rate for this reaction at 20 s will be $7 \times 10^{-3} \ M \ s^{-1}$.
- (3) The rate for this reaction at 80 s will be 1.75×10^{-3} M s⁻¹.
- (4) The [B] will be 0.35 M at t = 60 s.

31. For the reaction $A = \frac{k_1 \sec^{-1} \Delta}{k_2 \sec^{-1}} B$ following graph is given,

 $k_1 = 4 \times 10^{-2} \text{ sec}^{-1}$. Which is/are correct statement(s) $(\ln 2 = 0.7, \ln 8/7 = 0.14)$



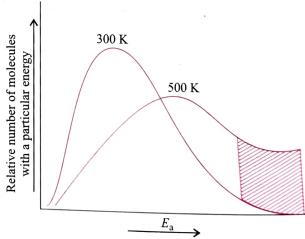
- (1) Equilibrium constant is 4.0
- (2) Time taken for the completion of 50% of equilibrium conc. of B is 14 sec.
- (3) Time taken for the completion of 10% of initial conc. of A is 2.8 sec.
- (4) Rate constant of backward reaction is $10^{-2} \, \mathrm{sec}^{-1}$

Energy of Activation, Effect of Temperature and Catalyst

- 32. Which of the following statement is (are) correct?
 - (1) Rate of reaction $\propto 1/E_a$
 - (2) At lower temperature increase in temperature causes more change in the value of k.
 - $(3) k = Ae^{-E_a/RT}$
 - (4) None of these
- 33. In a hypothetical reaction $X \to Y$, the activation energy for the forward and backward reactions is 15 and 9 kJ mol⁻¹, respectively. The potential energy of X is 10 kJ mol^{-1} . Then Plot of $t_{1/2}$ vs. concentration
 - (1) The heat of reaction is 6 kJ.
 - (2) The potential energy of Y is 16 kJ.
 - (3) The threshold energy of the reaction is 25 kJ.
 - (4) The reaction is endothermic.
- 34. The rate constant of a reaction is given by $k = 2.1 \times 10^{10}$ exp(-2700/RT). It means that
 - (1) log k versus 1/T will be a straight line with slope = $\frac{-2700}{2.303R}$.
 - (2) log k versus 1/T will be a straight line with intercept on log k axis = 2.1×10^{10} .
 - (3) The number of effective collisions are 2.1×10^{10} cm⁻³ s⁻¹.
 - (4) Half life of the reaction increases with increase of temperature.
 - 35. Which of the following relations are correct if ΔH represents only magnitude?
 - (1) Exothermic reactions: $E_{a(f)} + \Delta H = E_{a(b)}$
 - (2) Endothermic reactions: $E_{a(f)} = E_{a(b)} + \Delta H$
 - (3) Exothermic reactions: $\Delta H > E_a$
 - (4) Endothermic reactions: $\Delta H < E_a$
 - **36.** Which one is correct according to the collision theory of the rate of reaction?
 - (1) The threshold energy level is a characteristic of reaction.

- (2) The energy of activation decreases with rise in temperature.
- (3) The energy of adsorbed activated complex is lower than simple activated complex.
- (4) The energy of activated complex (both activated or adsorbed) is higher than reactant or product.
- 37. According to the collision theory, most molecular collisions do not lead to reaction. Which of the following is/are necessary for collisions to successfully lead to reaction?
 - (1) The total kinetic energy of the collision must be greater than some minimum value.
 - (2) A catalyst must be present at the collision.
 - (3) The colliding particles must be properly oriented in space when they collide.
 - (4) None of these
- **38.** Identify the true statement(s).
 - (1) A catalyst is chemically unchanged at the end of a reaction.
 - (2) A catalyst may appear in the kinetic rate equation of the reaction.
 - (3) A catalyst will not affect the composition of an equilibrium mixture.
 - (4) A catalyst cannot cause a non-spontaneous ($\Delta G > 0$) reaction to proceed.
- 39. Rate constant k varies with temperature by equation $\log k \, (\text{min}^{-1}) = \log 5 \frac{2000 \, \text{kcal}}{RT \times 2.303}$. We can conclude that
 - (1) The pre-exponential factor A is 10⁵.
 - (2) E_a is 2000 kcal
 - (3) E_a is 9.12 kcal
 - (4) The pre-exponential factor A is 5
- 40. The basic theory behind Arrhenius' equation is that
 - (1) The number of effective collisions is proportional to the number of molecules above a certain threshold energy.
 - (2) As the temperature increases, so does the number of molecules with energies exceeding the threshold energy.
 - (3) The rate constant is a function of temperature.
 - (4) The activation energy and pre-exponential factor are always temperature independent.
- 41. In Arrhenius equation, $k = A \exp\left(-\frac{E_a}{RT}\right)$. A may be termed as the rate constant at
 - (1) Very low temperature
 - (2) Very high temperature
 - (3) Zero activation energy
 - (4) The boiling temperature of the reaction mixture
- **42.** Select the correct statement(s).
 - (1) The order of a reaction may be changed with change in the experimental conditions.
 - (2) The rate of reaction, either exothermic or endothermic, both decreases with decrease in the temperature.
 - (3) A reaction mixture thermodynamically stable should be kinetically unstable.

- (4) A negative catalyst increases the energy of activation.
- 43. For a first order reaction,
 - (1) The degree of dissociation is equal to $(1 e^{-kt})$.
 - (2) A plot of reciprocal concentration of the reactant vs time gives a straight line.
 - (3) The time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of reaction.
 - (4) The pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1} .
- 44. Which of the following statement(s) is/are correct?
 - (1) The rate constant for the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2, \text{ is } 3.0 \times 10^{-5} \text{ s}^{-1}. \text{ If the rate is } \\ 2.40 \times 10^{-5} \text{ mol } L^{-1} \text{ s}^{-1}, \text{ then the concentration of } N_2O_5 \\ = 0.8 \text{ mol } L^{-1}.$
 - (2) In the Arrhenius equation, $k = A \exp(-E/RT)$, A may be termed as the rate constant at very low temperature.
 - (3) If I is the intensity of absorbed light and c is the concentration of AB for the photochemical process $AB + hv \rightarrow AB^*$, the rate of formation of AB* is directly proportional to I^2 .
 - (4) The rate constant, the activation energy, and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$, and $6.0 \times 10^{14} \text{ s}^{-1}$, respectively. The value of the rate constant as $T \to \infty$ is $6.0 \times 10^{14} \text{ s}^{-1}$.
- **45.** The distribution of molecular kinetic energy at two temperatures is as shown in the following graph:



Which of the following conclusions is/are correct?

- (1) The number of molecules with energy $E_{\rm a}$ or greater is proportional to the shaded area for each temperature.
- (2) The number of molecules with energy $E_{\rm a}$ or less is proportional to the shaded area for each temperature.
- (3) The number of molecules with energy $E_{\rm a}$ is the mean of all temperatures.
- (4) The graph follows the Maxwell-Boltzmann energy distribution law.
- **46.** In which of the following ways does an activated complex differ from an ordinary molecule?
 - (1) It is quite unstable and has no independent existence.
 - (2) $\Delta_f H^{\odot}$ is probably positive.

(3) The system has a greater vibrational character.

(4) The system has no vibrational character.

Linked Comprehension Type

paragraph.

The rate of reaction increases significantly with increase in The rate of Generally, rates of reactions and the rate of reactions. The rate. Generally, rates of reactions are doubled for every intemperature. Temperature cooperature remperature. Temperature coefficient gives us an idea 10°C rise in the rate of a reaction for 10°C the change in the rate of a reaction for every 10°C change in temperature.

Temperature coefficient (
$$\mu$$
) =
$$\frac{\text{Rate constant of } (T+10)^{\circ}\text{C}}{\text{Rate constant at } T^{\circ}\text{C}}$$

Arrhenius gave an equation which describes rate constant k as a function of temperature

$$k = Ae^{-E_a/RT}$$

where k is the rate constant, A is the frequency factor or preexponential factor, $E_{\rm a}$ is the activation energy, T is the temperature $\frac{1}{10}$ kelvin, and R is the universal gas constant.

Equation when expressed in logarithmic form becomes

$$\log k = \log A - \frac{E_{\rm a}}{2.303RT}$$

- 1. For a reaction $E_a = 0$ and $k = 3.2 \times 10^8 \text{ s}^{-1}$ at 325 K. The value of k at 335 K would be
 - (1) $3.2 \times 10^8 \text{ s}^{-1}$
- (2) $6.4 \times 10^8 \text{ s}^{-1}$
- (3) $12.8 \times 10^8 \text{ s}^{-1}$
- (4) $25.6 \times 10^8 \text{ s}^{-1}$
- 2. For which of the following reactions k_{310}/k_{300} would be maximum?
 - (1) $P + Q \longrightarrow R$; $E_a = 10 \text{ kJ}$
 - (2) E + F \longrightarrow D; $E_a = 21 \text{ kJ}$
 - (3) A + B \longrightarrow C; $E_a = 10.5 \text{ kJ}$
 - (4) L+M \longrightarrow N; $E_a = 5 \text{ kJ}$
- 3. Activation energies of two reactions are $E_{\rm a}$ and $E_{\rm a}'$ with $E_a > E_a'$. If the temperature of the reacting systems is increased from T_1 to T_2 (k' is rate constant at higher temperature).

(1)
$$\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$$
 (2) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$ (3) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$ (4) $\frac{k_1'}{k_1} > \frac{2k_2'}{k_2}$

4. For the given reactions, following data is given

$$P \rightarrow Q$$
 $k_1 = 10^{15} \exp\left(\frac{-2000}{T}\right)$

$$C \rightarrow D$$
 $k_2 = 10^{14} \exp\left(\frac{-1000}{T}\right)$

Temperature at which $k_1 = k_2$ is

(4) 868.44 K (1) 434.22 K (2) 1000 K (3) 2000 K

Paragraph 2

The reaction $S_2O_8^{2-} + 3I^{\odot} \longrightarrow 2SO_4^{2-} + I^{\odot}_3$ is of first order host. both with respect to persulphate and iodide ions. Taking the initial concentrations as a and b, respectively, and taking x as the concentration of the triodide at time t, a differential rate equation can be written.

Two suggested mechanisms for the reaction are:

I.
$$S_2O_8^{2-} + I^{\odot} \rightleftharpoons SO_4I^{\odot} + SO_4^{2-}$$
 (fast)
 $I^{\odot} + SO_4I^{\odot} \xrightarrow{k_1} I_2 + SO_4^{2-}$ (show)

$$I^{\odot} + I_2 \xrightarrow{k_2} I_3^{\odot}$$
 (fast)

II.
$$S_2O_8^{2-} + I^{\odot} \xrightarrow{k_1} S_2O_8^{3-} \text{ (slow)}$$

$$S_2O_8I^{3-} \xrightarrow{k_2} 2SO_4^{2-} + I^{\oplus}$$
 (fast)

$$I^{\oplus} + I^{\ominus} \xrightarrow{k_3} I_2 \text{ (fast)}$$

$$I_2 + I^{\odot} \xrightarrow{k_4} I_3^{\odot} \text{ (fast)}$$

5. The general differential equation for the above reaction is

(1)
$$\frac{dx}{dt} = k[a-x][b-3x] \quad (k>0)$$

(2)
$$\frac{dx}{dt} = -k[a-x][b-3x]$$
 $(k>0)$

(3)
$$\frac{dx}{dt} = k[a-x][b-x] \quad (k>0)$$

(4)
$$\frac{dx}{dt} = -k[a-x][b-x] \quad (k>0)$$

6. For the reaction $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{\odot}$

I.
$$\frac{-d[I_2]}{dt} = -\frac{1}{2} \frac{d[S_2 O_3^{2-}]}{dt}$$

II.
$$\frac{-d[I_2]}{dt} = -2 \frac{d[S_2O_3^{2-}]}{dt}$$

III.
$$\frac{-d[I_2]}{dt} = -2 \frac{d[I^{\odot}]}{dt} \times \frac{d[S_2O_3^{2-}]}{dt}$$

IV.
$$\frac{d[S_4O_6^{2-}]}{dt} = \frac{1}{2} \frac{d[I^{\odot}]}{dt}$$

The correct option is

(2) I and IV (3) II and IV (4) Only III (1) Only I

Paragraph 3

Consider the reaction represented by the equation:

$$CH_3Cl(g) + H_2O(g) \longrightarrow CH_3OH(g) + HCl(g)$$

These kinetic data were obtained for the given reaction concentrations:

Initial conc (M)		Initial rate of disappearance
[CH ₃ Cl]	$[H_2O]$	of CH ₃ Cl (M s ⁻¹)
0.2	0.2	1
0.4	0.2	2
0.4	0.4	8

- 7. The rate law for the reaction will be
 - (1) r = k[CH₃Cl][H₂O]
- (2) $r = k[CH_3Cl]^2[H_2O]$
- (3) $r = k[CH_3CI][H_2O]^2$
- (4) $r = k[CH_3Cl]^2[H_2O]^4$
- 8. Order with respect to [CH₃Cl] will be
 - (1) 0
- (2) 1
- (3)2
- (4) 3
- 9. Overall order of the reaction will be (2) 1
 - (1)0
- (3)2
- (4) 3

- 10. Unit of rate constant will be
 - $(1) s^{-1}$

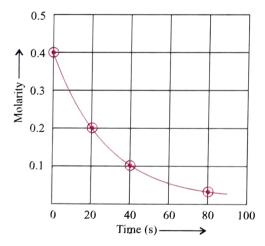
- (2) $L^2 \text{ mol}^{-2} \text{ s}^{-1}$
- (3) $L \text{ mol}^{-1} \text{ s}^{-1}$
- (4) mol L^{-1} s⁻¹
- 11. If H₂O is taken in large excess, the order of the reaction will
 - (1) 1
- (2)0
- (3) 3
- (4) 2

Paragraph 4

For the reaction: $aA + bB \longrightarrow cC + dD$

Rate =
$$\frac{dx}{dt} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

- 12. For reaction $3BrO^{\odot} \longrightarrow BrO_{2}^{\odot} + 2Br^{\odot}$, the value of rate constant at 80°C in the rate law for $-\frac{d[BrO^{\odot}]}{dt}$ was found to be $0.054 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$. The rate constant (k) for the reaction in terms of $\frac{d[BrO_3^{\odot}]}{dt}$ is
 - (1) $0.018 \text{ L mol}^{-1} \text{ s}^{-1}$
- (2) $0.162 \text{ L mol}^{-1} \text{ s}^{-1}$
- (3) $0.036 \text{ L mol}^{-1} \text{ s}^{-1}$
- (4) None of these
- 13. The rate of formation of SO₃ in the following reaction $2SO_2 + O_2 \longrightarrow 2SO_3$ is 100 g min⁻¹. Hence, the rate of disappearance of O₂ is
 - (1) 2 g min^{-1}
- $(2) 20 g min^{-1}$
- (3) 200 g min⁻¹
- $(4) 50 g min^{-1}$
- 14. A reaction follows the given concentration—time graph. The rate for this reaction at 20 s will be



- (1) $4 \times 10^{-3} \text{ M s}^{-1}$
- (2) $1 \times 10^{-2} \text{ M s}^{-1}$
- (3) $2 \times 10^{-2} \text{ M s}^{-1}$
- (4) $7 \times 10^{-3} \text{ M s}^{-1}$
- 15. In the following reaction,

$$xA \longrightarrow yB$$

$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3$$

where negative sign indicates rate of disappearance of the reactant. Thus, x : y is:

- (1)1:2
- (2) 2:1
- (3) 3 : 1
- (4) 3:10

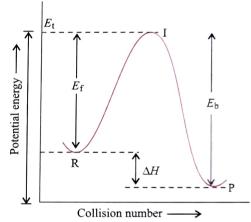
Paragraph 5

In the start of summer, a given sample of milk turns sour at room temperature (27°C) in 48 hours. In a refrigerator at 2°C, milk can be stored three times longer before it sours.

- 16. The activation energy of the souring of milk is (kJ mol⁻¹) (1) 30.210(2) 30.146 $(3)\ 30.0$ (4) 35.126
- 17. The time taken by the milk to sour at 37°C
 - (1) 35.2 hr (2) 32.5 hr
 - (3) 35.3 hr
- (4) 32.3 hr
- 18. Calculate the rate constant at 310 K, when rate constant at 300 K is 1.6×10^5
 - $(1) 2.363 \times 10^5$
- (2) 2.4×10^5
- $(3) 2.450 \times 10^5$
- $(4)\ 3.123 \times 10^5$

Paragraph 6

A collision between reactant molecules must occur with a certain minimum energy before it is effective in yielding product molecules. This minimum energy is called activation energy E_{s} . Larger the value of activation energy, smaller the value of rate constant k. Larger is the value of activation energy, greater is the effect of temperature rise on rate constant k.



 $E_{\rm f}$ = Activation energy of forward reaction

 $E_{\rm b}$ = Activation energy of backward reaction

$$\Delta H = E_{\rm f} - E_{\rm b}$$

 E_f = Threshold energy

- 19. If a reaction $A + B \longrightarrow C$ is exothermic to the extent of 30 kJ mol⁻¹ and the forward reaction has an activation energy of 249 kJ mol⁻¹ the activation energy for reverse reaction in kJ mol⁻¹ is
 - (1)324
- (2)279
- (3)40
- (4) 100
- 20. For the following reaction at a particular temperature, according to the equations

$$2N_2O_5 \longrightarrow 4NO_2 + O_3$$

$$2NO_2 + \frac{1}{2}O_2 \longrightarrow N_2O_5$$

The activation energies are E_1 and E_2 , respectively. Then

- (1) $E_1 \ge E_2$
- (2) $E_1 \leq E_2$
- (3) $E_1 = 2E_2$
- (4) $\sqrt{E_1 E_2^2} = 1$
- 21. In a hypothetical reaction $A \longrightarrow B$, the activation energies for the forward and backward reactions are 15 and 9 kJ mol⁻¹, respectively. The potential energy of A is 10 kJ mol⁻¹. Which of the following is wrong?

(1) The threshold energy of the reaction is 25 kJ.

- (2) The potential energy of B is 16 kJ.
- (3) The heat of reaction is 6 kJ.
- (4) The reaction is exothermic.

12. For two reactions, activation energies are E_{a1} and E_{a2} ; rate E_{a1} and E_{a2} ; rate For the same k_1 and k_2 at the same temperature. If $k_1 > k_2$,

- (2) $E_{a1} = E_{a2}$ $(1) E_{a1} > E_{a2}$
- $(3) E_{a1} < E_{a2}$
- (4) $E_{a1} \ge E_{a2}$

23. The rate constant of a certain reaction is given by $k = Ae^{-E_{\rm R}/RT}$

(where A = Arrhenius constant). Which factor should be lowered so that the rate of reaction may increase?

(1) T

(2) Z

(3) A

 $(4) E_a$

14. The activation energies for forward and backward reactions in a chemical reaction are 30.5 and 45.4 kJ mol⁻¹ respectively. The reaction is

- (1) Exothermic
- (2) Endothermic
- (3) Neither exothermic nor endothermic
- (4) Independent of temperature

Paragraph 7

The order of reaction is an experimentally determined quantity. It may be zero, positive, negative, or fractional. The kinetic equation of nth order reaction is

$$k \times t = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$
 ...(i)

Half life of nth order reaction depends on the initial concentration according to the following relation:

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$
 ...(ii)

The unit of the rate constant varies with the order but general relation for the unit of nth order reaction is

Unit of
$$k = \left[\frac{1}{\text{Conc}}\right]^{n-1} \times \text{Time}^{-1}$$
 ...(iii)

The differential rate law for nth order reaction may be given

$$\frac{dx}{dt} = k[A]^n \qquad \dots (iv)$$

where A denotes the reactant.

- 25. The unit of rate and rate constant are same for
 - (1) Zero order reaction
- (2) First order reaction
- (3) Second order reaction (4) Half order reaction

- 26. The rate constant for zero order reaction is
 - (1) $k = \frac{c_0}{2t}$
- $(2) k = \frac{c_0 c_t}{t}$
- (3) $k = \ln \frac{c_0 c_t}{2t}$
- (4) $k = \frac{c_0}{c}$

where c_0 and $c_{\rm t}$ are concentrations of reactants at respective

- 27. The half life for a zero order reaction equals
 - (1) $\frac{1}{2} \frac{k}{a^2}$ (2) $\frac{a^2}{2k}$ (3) $\frac{2k}{a}$ (4) $\frac{a}{2k}$

28. For a reaction:

$$I_{\Theta} + OCl_{\Theta} \longrightarrow IO_{\Theta} + Cl_{\Theta}$$

in an aqueous medium, the rate of the reaction is given by

$$\frac{d[\mathrm{IO}^{\odot}]}{dt} = k \frac{[\mathrm{I}^{\odot}][\mathrm{OCI}^{\odot}]}{[\mathrm{OH}]}$$

The overall order of the reaction is

- (2) 1(1) - 1
- (3) Zero
- (4)2
- 29. In a chemical reaction $A \longrightarrow B$, it is found that the rate of the reaction doubles when the concentration of A is increased four times. The order of the reaction with respect to A is:
 - (1) 0
- (2) $\frac{1}{2}$ (3) 1
- (4)2

Paragraph 8

A secondary alkyl halide (A) hydrolyzes with alkali (B) in aqueous medium simultaneously via S_N1 and S_N2 pathways with rate constants k_1 and k_2 , respectively. From kinetic data, it was found that a plot of = $\frac{-1}{[A]} \frac{d[A]}{dt}$ vs [B] is straight line with a slope equal to $2.7 \times 10^{-4} \text{ L mol}^{-1} \text{ min}^{-1}$ and intercept equal to 1.02×10^{-3} . Minimum initial concentration of [A] = 0.2 M and [B], i.e., [OH] = 0.5 M.

- 30. The value of overall rate constant of the hydrolysis of A (in L $mol^{-1} min^{-1}$) is
 - $(1) 2.7 \times 10^{-4}$
- (2) 1.02×10^{-3}
- $(3) 1.29 \times 10^{-3}$
- (4) None of these
- 31. The initial rate of consumption of isopropyl chloride (in M min^{-1}) is
 - $(1) 0.2 \times 10^{-3}$
- $(2) 2.3 \times 10^{-5}$
- $(3) 2.31 \times 10^{-4}$
- $(4) 2.31 \times 10^{-3}$

Paragraph 9

If a unimolecular reaction, $A(g) \longrightarrow Products$, takes place according to the mechanism

- 1. $A + A \stackrel{k_1}{\longleftarrow} A^* + A$
- II. $A^* \xrightarrow{k_2} P$

where k_1, k_{-1} , and k_2 are the rate constants and P, A, and A* stand for product molecule, normal molecules of reactants and activated molecules of reactants respectively.

32. Which of the following expressions are correct?

(1)
$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$$

$$(2) \frac{d[A^*]}{dt} = 0$$

(2)
$$\frac{d[A^*]}{dt} = 0$$
 (3) $[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$

(4) All of the above

33. Which of the following statements are correct?

- (1) At high pressure of A, i.e., high concentration of A, reaction obeys first order kinetics.
- (2) At low pressure of A, reaction follows first order kinetics.
- (3) The rate of reaction depends on both steps at all pressures.
- (4) All of the above statements are correct.

Paragraph 10

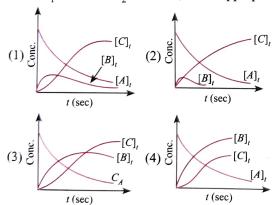
Two consecutive irreversible first order reaction can be represented by

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The rate equation for A is readily intergrated to obtain

$$[A]_t = [A]_0$$
. $e^{-k_1 t}$; and $[B]_t = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$

34. When $k_1 = 1 \text{ s}^{-1}$ and $k_2 = 500 \text{ s}^{-1}$; select appropriate graph



- 35. If k_1 and k_2 both are almost same then which graph in the above question is most suitable?
 - (1) Graph 1
- (2) Graph 2
- (3) Graph 3
- (4) Graph 4
- **36.** Select the correct statement for given reaction:
 - (1) A decrease linearly
 - (2) B rises to a maximum and then constant
 - (3) B rises to a maximum and then falls
 - (4) The slowest rate of increases of C occurring where B is maximum
- 37. At what time will B be present in maximum

$$(1) \ \frac{k_1}{k_2 - k_1}$$

$$(2) \ \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

(3)
$$\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$$

(4) None of these

Paragraph 11

An important parameter of a photochemical reaction is the qunatum efficinency or quantum yield (\$\phi\$) which is defined as

$$\phi = \frac{\text{moles of the substance reacted}}{\text{moles of photons absorbed}}$$

Absorption of UV radiation decompose acetone according to the reaction

$$(CH_3)_2CO \xrightarrow{hv} C_2H_6 + CO$$

- 38. If quantum yield is 0.8 then rate of formation of C₂H_c (mol/s) is:
 - (1) 2×10^{-8}
- (2) 1.6×10^{-9}
- (3) 16×10^{-9}
- $(4) 8 \times 10^{-9}$
- 39. The quantum yield of a reaction at $\lambda = 330$ nm is 0.4. A sample of acetone absorbs monochromatic radiation at $\lambda = 330$ nm at the rate of 7.2×10^{-3} Js⁻¹

(Given: $N_A = 6 \times 10^{23}$; $h = 6.6 \times 10^{-34}$ in S.I. unit). The rate of formation of CO(mol/s) is:

- $(1) 2 \times 10^{-8}$
- $(2) 8 \times 10^{-8}$
- $(3) 8 \times 10^{-9}$
- (4) None of these

Paragraph 12

Two competing irreversible first-order reaction are shown

$$A \xrightarrow{k_1} C$$

$$A \xrightarrow{k_2} D$$

where the stiochiometric coefficients are taken as unity. The rate law is

$$\left(\frac{d[A]}{dt}\right) = -k_1[A] - k_2[A] = -(k_1 + k_2)[A]$$

$$\Rightarrow$$
 [A] = [A]₀ $e^{-(k_1+k_2)t}$

For C, we have

$$\left(\frac{d[C]}{dt}\right) k_1[A] = k_1 [A]_0 e^{-(k_1 + k_2)}.$$

Multiplication by dt and integration from time 0 (where $[C]_0 = 0$) to an arbitary time t gives

$$[C] = \frac{k_1[A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t})$$

Similarly, integration of $\left(\frac{d[D]}{dt}\right)$ gives

$$[D] = \frac{k_2[A]_0}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t})$$

The sum of the rate constants $k_1 + k_2$ appears in the exponentials for both [C] and [D].

At any time we also have
$$\frac{[C]}{[D]} = \frac{k_1}{k_2}$$

starting initially with only 'X', ratio
$$\frac{[X]_t}{[Y]_t + [Z]_t}$$

$$(1) [A]_0 (e^{kt}-1)$$

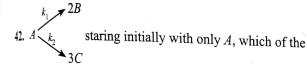
$$(2) \frac{1}{(e^{kt}-1)}$$

- (3) Depends upon initial concentration of X
- (4) Independent of time



Starting with pure A ratio of rate of production of B to C is:

- (1) Independent of time
- (2) Independent of mechanism of reaction
- (3) Depends upon initial concentration of A
- (4) Independent of temperature



following is correct at time t?

$$(1) [A]_0 = \frac{2}{3} [A]_t + [B]_t + [C]_t$$

(2)
$$[A]_0 = [A]_t + 2[B]_t + 3[C]_t$$

(3)
$$[A]_0 = [A]_t + \frac{[B]_t}{2} + \frac{[C]_t}{3}$$

$$(4) [A]_0 = [A]_t + [B]_t + [C]_t$$

Matrix Match Type



This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

Column I (Half life)		Column II (Order)
$t_{1/2} = \text{constant}$	p.	First order
$t_{1/2} \propto a$	q.	Pseudo first order
c. $t_{1/2} \propto p^{-1}$	r.	Zero order
$\mathbf{d.} \ t_{1/2} \propto 1/a$	S.	Second order

where a = initial concentration of the reactant and b = initial pressure of the reactant.

2.

	Column I (Kinetic equation)		Column II (Unit of rate constant)
a.	x = kt	p.	$L \text{ mol}^{-1} \text{ s}^{-1}$
b.	$k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{(a)} \right]$	q.	s ⁻¹
c.	$k = \frac{2.303}{t} \log \left(\frac{a}{a - x} \right)$	r.	atm ⁻¹ s ⁻¹
d.	$k = \frac{2.303}{t(a-b)} \log \left[\frac{b(a-x)}{a(b-x)} \right]$	s.	$\mathrm{mol}\;\mathrm{L}^{-1}\;\mathrm{s}^{-1}$

3.

	Column I		Column II		Column III
a.	x is plotted against t in zero order reaction	p.	Slope = $-k/2.303$	u.	Intercept = 0
b.	log(a-x) is plotted against t in first order reaction	q.	Slope = $2k$	V.	Intercept = 1/a
c.	$(a-x)^{-1}$ is plotted against t in second order reaction	r.	Slope = $-k$ (when log is natural)	w.	Intercept = $1/a^2$
d.	$(a-x)^{-2}$ is plotted against t in second order reaction	s.	Slope = $-k$	x.	Intercept = $\log a$

4. Column I (First order reaction)

a. [A] versus time

p. $t \longrightarrow t$ b. $-\frac{d[A]}{dt}$ versus [A]

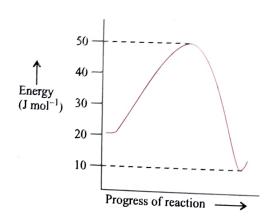
q.

c.	$-\frac{d[A]}{dt}$ versus time	r.	
d.	log [A] versus time	s.	1>

5.

·			
	Column I		Column II
a.	$ \begin{array}{c} \uparrow \\ t_{1/2} \\ \hlinec_0 \longrightarrow \end{array} $	p.	$t_{\infty} = 2 \times t_{1/2}$
b.	$ \uparrow_{1,2} \\ \hline $	q.	$t_{3/4} = 2 \times t_{1/2}$
c.	$ \uparrow \frac{1}{c_t} $ Time \rightarrow	r.	$ \begin{array}{c} $
d.		S.	$t_{1/2} \times c_0 = \text{consant}$
		t.	Zero order

6.



	Column I		Column II
a.	$E_{\mathbf{a}}(\mathbf{f})$	p.	
b.	$E_{\rm a}({\rm b})$	q.	40 kJ mol ⁻¹
c.	$\Delta_{_{ m f}} H$	r.	30 kJ mol ⁻¹
d.	$E_{ m Threshold}$	s.	50 kJ mol ⁻¹

7.

	Column I		Column II
a.	Ester + NaOH→ Alcohol + Salt	p.	$k = Ae^{-E_a/RT}$
b.	$2H_2O_2 \longrightarrow 2H_2O + O_2$	q.	Concentration
c.	$2NH_3 \xrightarrow{\text{Au} \atop \text{Zero}} N_2 + 3H_2$	r.	Rate
d.	Sucrose $+ H_2O \longrightarrow$ Glucose $+$ Fructose	S.	$t_{1/2} = x$ minutes at a consant temperature at any time of the reacti

	Column I		Column II
a.	Sucrose in aqueous solution of dilute acid is hydrolyzed to glucose and fructose.	p.	Bimolecular
b.	<i>n</i> -Propyl bromide in ethanolic solution gives ethyl propyl ether	q.	Pseudo unimolecular reaction
c.	Benzyl bromide is converted into benzylthiol via carbocationic intermediate formation mechanism.	r.	Unimolecular
d.	The reaction: $2O_3 \longrightarrow 3O_2$ follows the mechanism.	s.	First order
	I. $O_3 \rightleftharpoons O_2 + O$ (Fast) II. $O_3 + O \longrightarrow 2O_2$ (Slow)		

9.

	Column I		Column II
100000000000000000000000000000000000000	Collision theory	p.	Mol L ⁻¹ s ⁻¹
b.	Zero order reaction	q.	Bimolecular reaction
c.	Photochemical reaction	r.	Fractional
d.	Intercept (in Arrhenius plot)	s.	ln A
e.	Order of reaction	t.	Zero order reaction

Chemical Kinetics 4.119

[Answer the question given below by appropriately matching the information given in three column of the following

	pseudo molecular reaction		Units of rate constant (k') for pseudo		Value of k'
a	<u>Pseudo unimolecular reaction:</u>	-	reaction		
	1 st order kinetics, molecularity of reaction = 2.	i	$ m L^3~mol^{-3}~s^{-1}$	p	0.2×10^{-4}
	Example: - Hydrolysis of ester				
	RCOOR' + $H_2O \xrightarrow{H^{\oplus}}$ RCOOH + R'OH [H_2O] (<i>i.e.</i> , solvent) remains nearly constant during the course of reaction and [H_2O] = 55M. Rate constant (k) = 1.1×10^{-3} s ⁻¹				
,	Pseudo unimolecular reaction:	ļ	-		
	1 st order kinetics, molecularity of reaction = 3.	ii	L mol ⁻¹ s ⁻¹	q	0.2×10^{-3}
	Example :- Preparation of esters from anhydride and alcohol. (RCO) ₂ O + 2 R'OH 2 RCOOR' + H ₂ O (Solvent)				
	[Solvent] remains nearly constant during the course of reaction and [R'OH] = 10 M. Hypothetical rate constant (k) = 2.0×10^{-4} s ⁻¹		,		
2	Pseudo bimolecular reaction:	iii	L ² mol ⁻² s ⁻¹	r	0.2 × 10 ⁻⁶
	2 nd order kinetics, molecularity of reaction = 3		L mor s	1	0.2 × 10 °
	Example :- Saponification of ester.	4 .30	1 =		
	$RCOOR' + NaOH \xrightarrow{H_2O} RCOONa + R'OH$				
	[H ₂ O] (<i>i,e,</i> .solvent) remains nearly constant during the course of reaction and [H ₂ O] = 55 M. Hypothetical rate constant (k) = 1.1×10^{-2} L mol ⁻¹ s ⁻¹		17 20-25 20-36		
d	Pseudo bimolecular reaction:				0.2×10^{-5}
	2 nd order kinetics, molecularity of reaction = 4		7	S	0.2 × 10 -
	Example:- Hypothetical reaction:				
	$A + B + 2C$ (solvent) \longrightarrow $P + Q$				
	[Solvent] remains nearly constant during the course of reaction and [solvent] or $[C] = 10M$.				
	Hypothetical rate constant (k) = $2.0 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$				

- 10. The correct combination for the pseudo reaction with molecularity = 2 is:
 - (1) a—ii—p
- (2) a—iii—p
- (3) a—iii—q
- (4) a—i—r
- 11. The correct combination for the pseudo reaction with molecularity = 3 is:
 - (1) b—ii—p
- (2) b—iii—s
- (3) $b_{-i}q$
- (4) b—iii—q
- 12. The only incorrect combination for pseudo bimolecular reaction with molecularity = 3 is:
 - (1) a—ii—p
- (2) b—iii—s
- (3) c—iii—q
- (4) c-i-r
- 13. The correct combination for pseudo bimolecular reaction with molecularity = 4 is:
 - (1) d-i-r
- (2) d—ii—p
- (4) d—iii—s
- (4) d—iii—q

Numerical Value Type

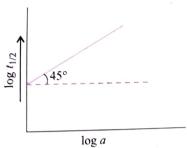
- 1. The half-life period of a radioactive element is 40 days. If 32 g of this element is stored for 160 days, calculate the weight of the element that would remain in gram.
- 2. If one starts wth 1 Curie (Ci) of radioactive substance $(t_{1/2} = 15 \text{ hr})$, the activity left after a period of two weeks will be about $0.02x \mu Ci$. Find the value of x.
- 3. If 80% of a radioactive element undergoing decay is left over after a certain period of time t from the start, how many such periods should elapse from the start for just over 50% of the element to be left over?
- 4. Hydrolysis of an alkyl halide (RX) by dilute alkali [OH] takes place simultaneously by SN^2 and SN^1 pathways.

A plot of $-\frac{1}{[RX]} \frac{d[R-X]}{dt}$ vs [OH] is a straight line of the

slope equal to $2 \times 10^3 \text{ mol}^{-1} \text{ L h}^{-1}$ and intercept equal to $1 \times 10^2 \text{ h}^{-1}$. Calculate the initial rate (mole $L^{-1} \text{ min}^{-1}$) of consumption of RX when the reaction is carried out taking

1 mol L^{-1} of RX and 0.1 mol L^{-1} of $[\overset{\hookrightarrow}{OH}]$ ions.

5. Following is the graph between $\log t_{1/2}$ and $\log a$ (*a* initial concentration) for a given reaction at 27°C.



Find the order of reaction.

- 6. For the reaction A → Products, it is found that the rate of reaction increases by a factor of 6.25 when concentration of A increases by a factor of 2.5. Calculate the order of reaction with respect to A.
- 7. In the case of a first order reaction, the time required for 93.75% of reaction to take place is x times that required for half of the reaction. Find the value of x.
- **8.** For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, the experimental rate expression is $-dc/dt = k[NO_2]^2$. Find the number of molecules of CO involved in the slowest step.
- Following are two first order reactions with their half times given at 25°C.

A
$$\xrightarrow{t_{1/2} = 30 \text{ min}}$$
 Products

B
$$\xrightarrow{t_{1/2} = 40 \text{ min}}$$
 Products

The temperature coefficients of their reaction rates are 3 and 2, respectively, between 25°C and 35°C. If the above two reactions are carried out taking 0.4 M of each reactant but at different temperatures: 25°C for the first order reaction and 35°C for the second order reaction, find the ratio of the concentrations of A and B after an hour.

Consider the following statements for a second order reaction and score of each statement.

$$2A \rightarrow P$$

		Score
a.	$[A] = \frac{[A_0]}{1 + kt}$	3
	A plot of 1/[A] ² vs time will be straight line	2
c.	Half life is long when the concentration is low	1

Find the total score of the correct statements.

- 11. Two substances $A(t_{1/2} = 5 \text{ min})$ and $B(t_{1/2} = 15 \text{ min})$ follow first order kinetics and are taken in such a way that initially [A] = 4[B]. The time after which the concentration of both the substance will be equal is 5x min. Find the value of x.
- 12. The initial concentrations of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 30 s. How much time will be taken in 20% completion of the reaction?
- 13. A second order reaction requires 70 min to change the concentration of reactants from 0.08 M to 0.01 M. The time required to become 0.04 M = 2x min. Find the value of x.
- 14. For the reaction:

$$H_2 + Cl_2 \xrightarrow{Sunlight} 2HCl$$
 taking place on water. Find the order of reaction.

- 15. What is the order of reaction for which rate becomes half if volume of the container having same amount of reactant is doubled? Assume gaseous phase reaction.
- **16.** The half-life period of a reaction, becomes 32 times when reactant concentration is doubled. The order of reaction is
- 17. A straight line was obtained on plotting $\log \frac{dx}{dt}$ vs.

$$\log (a-x)^n$$
 with an intercept on $\log \left(\frac{dx}{dt}\right)$ axis to 0.48.

The rate constant for the reaction is in litreⁿ⁻¹ mol¹ t^{-1}

- **18.** If the rate of reaction is 2.0×10^{-3} mol L⁻¹ s⁻¹ at 50°C and 1.6×10^{-2} mol L⁻¹ s⁻¹ at 80°C, then what will be the temperature coefficient of the reaction?
- 19. The half lives of two parallel path reaction A C are 5 hrs and 20 hrs respectively. The average half-life for the decay of A is
- **20.** A reaction occurs in 'n' parallel paths. For each path having energy of activation as E, 2E, 3E,..., nE and rate constant K, 2K, 3K, ..., nK respectively. If $E_{AV} = 3.66 E$ then n is

Archives

JEE MAIN

Single Correct Answer Type

- 1. The half-life period of a first order chemical reaction is 6.93 min. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301)
 - (1) 230.3 min
- (2) 23.03 min
- (3) 46.06 min
- (4) 460.6 min

- 2. The time for half-life period of a certain reaction, $A \longrightarrow$ products is 1 h. When the initial concentration of the reactant A is 2.0 mol L⁻¹, how much time does it take for its concentration to come from 0.50 to 0.25 mol L⁻¹, if it is a zero-order reaction?
 - (1) 4 h
- (2) 0.5 h
- (3) 0.25 h
- (4) 1 h
- (AIEEE 2010)

3, Consider the reaction, C_{0}^{OUD} $H_2S(aq) \longrightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$

The rate equation for this reaction is,

$$\frac{\text{he rate equal}}{\text{Rate}} = k[\text{Cl}_2] [\text{H}_2\text{S}]$$

Which of these mechanisms is/are consistent with this rate

equation?
(I)
$$Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^- \text{ (slow)}$$

$$\frac{Cl_2 + H_2S}{Cl^+ + HS^-} \longrightarrow H^+ + Cl^- + S \text{ (fast)}$$

$$(I) H_2 S \rightleftharpoons H^+ + HS^- \text{ (fast equilibrium)}$$

$$\frac{10^{1} \text{ H}_2\text{ S}}{\text{Cl}^+ + \text{HS}^-} \longrightarrow 2\text{Cl}^- + \text{H}^+ + \text{S (slow)}$$

(2) Both (I) and (II)

(3) Neither (I) nor (II) (4) (I) only

(AIEEE 2010)

4. A reactant A forms two products

 $A \xrightarrow{k_1} B$, Activation energy E_a

 $A \xrightarrow{k_2} C$, Activation energy E_{a_3}

If $E_{a_2} = 2E_{a_1}$ then k_1 and k_2 are related as

$$(2) k_1 = k_2 e^{E_{a_1}/RT}$$

(1)
$$k_1 = 2k_2 e^{E_{a_2}/RT}$$
 (2) $k_1 = k_2 e^{E_{a_1}/RT}$ (3) $k_2 = k_1 e^{E_{a_2}/RT}$ (4) $k_1 = Ak_2 e^{E_{a_1}/RT}$

(AIEEE 2011)

5. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about

(1) 10 times

(2) 24 times

(3) 32 times

(4) 64 times

(AIEEE 2011)

6. For a first order reaction $A \rightarrow \text{products}$, the concentration of A changes from 0.1 M to 0.025 M in 40 min. The rate of reaction when the concentration of A is 0.01 M is

(1) 1.73×10^{-5} M/min (2) 3.47×10^{-4} M/min

(3) 3.47×10^{-5} M/min (4) 1.73×10^{-4} M/min

(AIEEE 2012)

7. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \text{ and } \log 2 = 0.301)$:

(1) $53.6 \text{ JK}^{-1} \text{ mol}^{-1}$

(2) $48.6 \text{ JK}^{-1} \text{ mol}^{-1}$

(3) $58.5 \text{ JK}^{-1} \text{ mol}^{-1}$

(4) $60.5 \text{ JK}^{-1} \text{ mol}^{-1}$

(JEE Main 2013)

8. For the non-stoichiometric reaction,

 $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concen- tration of A	Initial concen- tration of B	Initial rate of formation of C	
0.1 M	0.1 M	1.2×10^{23}	
0.1 M	0.2 M	1.2×10^{23}	
0.2 M	0.1 M	2.4×10^{23}	

The rate of law for the formation of C is

(1)
$$\frac{dC}{dt} = k[A][B]$$

(1)
$$\frac{dC}{dt} = k[A][B]$$
 (2) $\frac{dC}{dt} = k[A]^2[B]$

(3)
$$\frac{dC}{dt} = k[A][B]^2 \qquad (4) \frac{dC}{dt} = k[A]$$

$$(4) \ \frac{dC}{dt} = k[A]$$

(**JEE Main 2014**)

- **9.** Higher order (> 3) reactions are rare due to
 - (1) low probability of simultaneously collision of all the reacting species
 - (2) increase in entropy and activation energy as more molecules are involved
 - (3) shifting of equilibrium towards reactants due to elastic collisions
 - (4) loss of active species on collision

(JEE Main 2015)

- 10. Decomposition of H₂O₂ follows a first-order reaction. In fifty minutes the concentration of H2O2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be:
 - (1) 1.34×10^{-2} mol min⁻¹ (2) 6.93×10^{-2} mol min⁻¹
 - (3) $6.93 \times 10^{-4} \text{ mol min}^{-1}$ (4) 2.66 L min^{-1} at STP

(**JEE Main 2016**)

11. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol⁻¹. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then $\ln (k_2/k_1)$ is equal to: $(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$

(1) 8

(2) 12

(3) 6

(4) 4

(JEE Main 2017)

- 12. At 518° C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s⁻¹ when 5% had reacted and 0.5 Torr s⁻¹ when 33% had reacted. The order of the reaction is:
 - (1) 3

(2) 1

(3) 0

(4) 2

(JEE Main 2018)

JEE ADVANCED

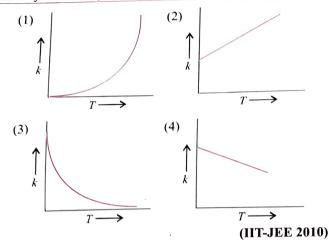
Single Correct Answer Type

- 1. For a first order reaction $A \rightarrow P$, the temperature (T)dependent rate constant (k) was found to follow the equation $\log k = -2000(1/T) + 6.0$. The pre-exponential factor A and the activation energy E_a , respectively, are
 - (1) $1.0 \times 10^6 \text{ s}^{-1}$ and 9.2 kJ mol^{-1}
 - (2) 6.0 s^{-1} and 16.6 kJ mol^{-1}
 - (3) $1.0 \times 10^6 \text{ s}^{-1}$ and 16.6 kJ mol^{-1}
 - (4) $1.0 \times 10^6 \text{ s}^{-1}$ and 38.3 kJ mol⁻¹

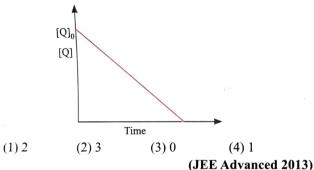
(IIT-JEE 2009)

2. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows the Arrhenius equation is

4.122 Physical Chemistry



3. In the reaction, P + Q → R + S
the time taken for 75% reaction of P is twice the time taken
for 50% reaction of P. The concentration of Q varies with
reaction time as shown in the figure. The overall order of
the reaction is



4. For the elementary reaction M→N, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is

(1)4

(2) 3

(3) 2

(4) 1

(JEE Advanced 2014)

Multiple Correct Answers Type

1. For the first order reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

- (1) The concentration of the reactant decreases exponentially with time.
- (2) The half life of the reaction decreases with increasing temperature.
- (3) The half life of the reaction depends on the initial concentration of the reactant.
- (4) The reaction proceeds to 99.6% completion in 8 half-life durations. (IIT-JEE 2011)
- 2. According to the Arrhenius equation,
 - (1) A high activation energy usually implies a fast reaction.
 - (2) Rate constant increases with increase in temperature. This is due to greater number of collisions whose energy exceeds the activation energy.

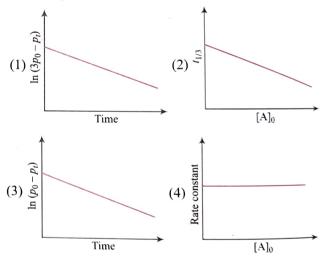
- (3) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant.
- (4) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

(JEE Advanced 2016)

- 3. In a bimolecular reaction, the steric factor P_{was} experimentally determined to be 4.5. The correct option(s) among the following is(are)
 - (1) The activation energy of the reaction is unaffected by the value of the steric factor.
 - (2) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
 - (3) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used
 - (4) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally.

(JEE Advanced 2017)

4. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning (t = 0) and at time t are P_0 and P_t , respectively. Initially only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach $1/3^{rd}$ of its initial value. The correct options(s) is (are) (Assume that all these gases behaves as ideal gases)



(JEE Advanced 2018)

Numerical Value Type

1. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data were obtained. What is the order of the reaction?

[R] (mol)	1.0	0.75	0.40	0.10
T (min)	0.0	0.05	0.12	0.18

(IIT-JEE 2010)

2. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$, respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? $(\log_{10} 2 = 0.3)$

(HT-JEE 2012)

Consider the following reversible reaction,

 $A(g) + B(g) \rightleftharpoons AB(g)$

2012)

The activation energy of the backward reaction exceeds The action exceeds that of the forward reaction by 2RT (in J mol⁻¹). If the preexponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG° (in J mol⁻¹) for the reaction at 300 K is

(Give; ln(2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy)

(JEE Advanced 2018)

Answers Key

cXE	RCISES				186. (4)	187. (4)	188. (2)	189. (4)	190. (3)
t ha	gle Correct Answer Ty	pe			191. (1)	192. (4)	193. (1,3)	194. (4)	195. (3)
	5 (1)	3. (3)	4. (4)	5. (4)	196. (1)	197. (4)	198. (2)	199. (2)	200. (4)
	$\frac{1}{2}$ $\frac{2}{2}$ $\frac{1}{2}$ $\frac{1}$	8. (3)	9. (3)	10. (3)	201. (2)	202. (2)	203. (4)	204. (2)	205. (1)
	0. (2)	13. (3)	4.4.	15. (3)	206. (2)	207. (4)	208. (3)	209. (3)	210. (1)
	1. (3)		- 67	20. (3)	211. (2)	212. (2)	213. (3)	214. (4)	215. (3)
	(b, (1)			25. (3)	216. (4)	217. (3)	218. (1)	219. (4)	220. (2)
	11. (2)			30. (2)	221. (1)	222. (3)	223. (3)	224. (1)	225. (2)
	ju. (1)			35. (4)	226. (1)	227. (1)	228. (3)	229. (3)	230. (4)
	JI (1)	38. (4)	39. (3)	40. (4)	231. (3)	232. (3)	233. (2)	234. (3)	235. (1)
	30 (1)	43. (1)	44. (2)		236. (4)	` ,	238. (3)	239. (3)	240. (3)
2	· (1)	48. (1)	49. (4)	45. (4)	241. (1)		243. (4)	244. (4)	245. (4)
f	46. (3) 47. (1) 51. (1) 52. (1)	53. (2)	54. (2)	50. (1)	246. (3)		248. (2)	249. (2)	250. (2)
at	56. (3) 57. (1,2,3)			55. (4)	251. (3)		253. (3)	254. (2)	255. (1)
1	61. (4) 62. (2)	63. (3)	64. (4)	60. (4) 65. (2)	256. (2)	257. (2)	258. (4)	259. (3)	260. (3)
1	66. (2) 67. (1)	68. (1)	69. (1)	70. (1)	Multiple (Correct Answ	ers Type		
	71. (2) 72. (4)	73. (2)	74. (2)	75. (3)	1. (3,	1) 2.	(3, 4)	3. (1, 2, 3, 4	4) 4. (1, 2, 3, 4)
	76. (2) 77. (2)	78. (1)	7 9. (4)	80. (3)	5. (2)		(1, 2, 3)	7. (4)	8. (2, 3, 4)
	81. (3) 82. (2)	83. (2)	84. (1)	85. (2)	9. (1, 1		(1, 2)	11. (1,2,3,4)	12. (1, 2, 3, 4)
	86. (3) 87. (2)	88. (3)	89. (2)	90. (2)	13. (1, 2	2) 14.	(1, 2, 3)	15. (1,2,3,4)	16. (1, 2, 3, 4)
	91. (2) 92. (3)	93. (3)	94. (4)	95. (2)	17. (1, 1		(3, 4)	19. (2, 3)	20. (1, 2, 3)
	%. (1) 97. (1)	98. (2)	99. (1)	100. (1)	21. (3,			23. (1, 2)	24. (1, 3, 4)
	101. (3) 102. (2)	103. (1)	104. (4)	105. (2)	25. (1,			27. (2, 3)	28. (1, 2, 3, 4)
	106. (4) 107. (1)	108. (1)	109. (1)	110. (1)	29. (1,				32. (1, 2, 3)
	¹¹¹ . (2) 112 . (4)	113. (1)	114. (3)	115. (2)	33. (1, 37. (1,				36. (1, 2, 3, 4)
-	^{116.} (2) 117. (1)	118. (3)	119. (2)	120. (4)	41. (2,		(1,2,3,4) $(1,2)$		40. (1, 2, 3, 4)
•	¹²¹ . (1) 122 . (4)	123. (2)	124. (3)	125. (2)	45. (1,		(1, 2) $(1, 3)$	43. (1, 4)	44. (1, 4)
018)	126. (3) 127. (4)	128. (3)	129. (2)	130. (4)					
	¹³¹ . (4) 132 . (2)	133. (3)	134. (3)	135. (2)	1. (1)	omprehensio			
sured	136. (2) 137. (2)	138. (2)	139. (3)	140. (2)	6. (2)	(-)	3. (3)	4. (1)	5. (1)
ined.	141. (2) 142. (4)	143. (3)	144. (1)	145. (2)	11. (1)	(-)	8. (2)	9. (4)	10. (2)
	146. (3) 147. (3) 151. (3) 152. (3)	148. (1)	149. (3)	150. (4)	16. (2)	()	13. (2) 18. (1)	14. (4)	15. (2)
	151. (3) 152. (3) 156. (1) 157. (3)	153. (1)	154. (3)	155. (1)	21. (4)	()	23. (4)	19. (2)	20. (1)
.40)	¹⁰¹ . (1) 162 (2)	162 (2)	159. (1) 164. (4)	160. (1) 165. (3)	26. (2)		28. (2)	24. (1) 29. (2)	25. (1)
2010) sition.	167 (2)	1(0 (2)			31. (3)	. ,	33. (4)	34. (2)	30. (3)
sition of its	(4) 172 (4)	153 (1)			36. (3)		38. (3)	39. (3)	35. (3) 40. (2)
yhat is	(3) 177 (1	150 (4)		/ 12	41. (1	42. (3)		(-)	10. (2)
VIIa	¹⁸¹ . (4) 182. (4)	(1) 183. (2)							
		` ′							

Matrix Match Type

Q.No.	a	b	c	d	e	f
1.	p, q	r	p, q	r, s		
2.	s	p, r	q	p, r		_
3.	s, u	p, r, x	s, v	q, w		_
4.	r	q	r	p		
5.	q	p, s, t	s	p, r, t	_	
6.	r	q	р	s		_
7.	p	p, r, s	p, q	p, r, s	_	
8.	p, q, s	p	r, s	p, s	_	
9.	q	p	t	s	r	

10. (1) 11. (2) **12.** (4)

13. (1)

9. (2)

Numerical Value Type

1. (2) **6.** (2) **2.** (9) 7. (4) **3.** (3)

4. (5) **5.** (0)

8. (0)

10. (4)

11. (3) **12.** (5) **13.** (5)

14. (0)

15. (1)

17. (3) **16.** (6)

18. (3)

19. (4)

20. (5)

ARCHIVES

JEE Main

Single Correct Answer Type

1. (3) **2.** (3)

3. (4)

4. (2)

5. (3)

7. (1) **6.** (2)

8. (4)

9. (1) **10.** (3)

12. (4) **11.** (4)

JEE Advanced

Single Correct Answer Type

1. (4) **2.** (1) **3.** (4)

4. (2)

Multiple Correct Answers Type

1. (1, 2, 4)

2. (2, 3, 4) **3.** (2, 4)

4. (1, 4)

Numerical Value Type

1. (0)

2. (9)

3. (8500)

Surface Chemistry

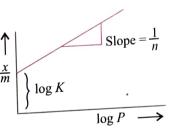
OVERVIEW

- Laksorption is a phenomenon of attracting and retaining the Adsorption of a substance at the surface of a solid or liquid rather than in bulk.
- 2. Adsorbate are the molecular species which concentrate at
- 3. The material on the surface of which adsorption takes place is called adsorbent.
- 4. If the concentration of adsorbate is more on the surface with respect to bulk, it is called positive adsorption. If it is less on the surface with respect to bulk it is called negative adsorption.
- 5. Greater the surface area of the adsorbent, greater is the adsorption.
- 6 Higher the critical temperature of a gas, greater is its adsorption.
- 7. Physical adsorption is due to van der Waals forces and is reversible. Chemisorption involves the formation of compounds on the surface and is irreversible.
- & At constant temperature, adsorption generally increases with pressure. Lower the temperature, greater is the effect of pressure.
- Freundlich adsorption isotherm is

$$\frac{x}{m} = KP^{1/n} \ (n > 1)$$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P \quad \log \frac{x}{m}$$

i.e., plot of $\log x/m$ vs \log P gives a straight line with slope = 1/n and intercept $= \log K$.



Slope = $\frac{1}{a}$

10. Langmuir adsorption isotherm is

$$\frac{x}{m} = \frac{aP}{1 + bP}$$

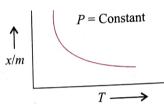
where a and b are $\log \frac{m}{x}$ constants. constants.

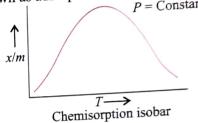


 $1/P \longrightarrow$ A plot of $\log m/x$ against 1/P gives a straight line with slope = 1/a and intercept = b/a.

11. Adsorption is generally temperature dependent. Most of the adsorption processes are exothermic and therefore adsorption decreases with increasing temperature.

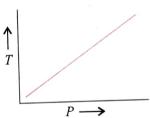
Adsorption isobars: A graph drawn between the degree of adsorption (x/m) and temperature (T) at a constant pressure of adsorbate gas is known as adsorption isobar. P = Constant





Physisorption isobar

Adsorption isostere: The plot of temperature versus pressure for a given amount of adsorption is called adsorption isostere.



- 12. Colloids are classified in the following three different ways:
 - a. Based on the physical state of the dispersed phase and dispersion medium, there are 8 types (except gas in gas)
 - Based on the nature of interaction between dispersed phase and dispersion medium, i.e., as lyophilic and lyophobic colloids.
 - c. Based on the types of particles of the dispersed phase i.e., as multimolecular, macromolecular, and associated colloids.
- 13. Lyophilic sols are formed by organic substances such as starch, gum, proteins, etc. These are reversible. Lyophobic sols are formed by inorganic substances such as metals, their sulphides, etc. They are irreversible.

Lyophilic sols are more stable than lyophobic due to their greater hydration in the solution.

14. Colloidal dispersions of sulphur, gold, etc., are multimolecular. Those of polymers, e.g., starch, cellulose, proteins, nylon, rubber, etc., are macromolecular while a collodal sol of soap in water is associated colloid.

- 15. The aggregate of ions in an associated colloidal solution is called ionic micelle. The concentration above which these ionic micelles are formed is called critical micellization concentration (CMC) and the temperature above which they are formed is called Kraft temperature (T_K) .
- 16. Collodion is a lyophilic colloidal sol of cellulose nitrate in ethyl alcohol.
- 17. Conversion of a freshly precipitated substance into colloidal sol by shaking with a suitable electrolyte is called peptization, e.g., Fe(OH), ppt with FeCl, sol, AgI ppt with AgNO, or KI solution. The electrolyte should have a common ion.
- 18. According to Hardy Schulze rule, greater the valency of the oppositely charged ions of the electolyte, faster is the coagulation. The coagulating power of the ion is directly proportional to the fourth power of its valency. Thus, for a negatively charged sol, $Al^{3+} > Ba^{2+} > Na^{\oplus}$. For a positively charged sol, $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{\odot}$
- 19. Isoelectric point of colloids: The H[®] ions concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e., they are electrically neutral) is known as isoelectric point of colloid.
- 20. The conversion of a freshly precipitated substance into colloidal solution by shaking with a suitable electrolyte is called peptization.
- 21. The movement of colloidal particles under the influence of an electric field is called electrophoresis.
- 22. The process of changing the colloidal particles in a solution into an insoluble preciptate by the addition of some suitable electolytes is known as coagulation.
- 23. The minimum number of millimoles of the electrolyte required for complete coagulation of one litre of a colloidal solution is called its coagulation or flocculation value.
- 24. The minimum number of milligrams of a lyophilic solution needed to protect 10 mL of gold solution by the addition of 1 mL of 10% NaCl is called gold number. Protective power is the reciprocal of gold number.
- 25. The colligative property used to determine the molecular masses of colloidal is called osmotic pressure.
- 26. The zig-zag movement of the colloidal particles in a colloidal sol is called Brownian movement.
- 27. The scattering of light by colloidal particles is called Tyndall
- 28. A colloidal sol is a stable because all the colloidal particles in a colloidal sol carry the same charge.
- 29. A colloidal sol can be purified i.e., particles of the crystalloids can be separated from it by dialysis or ultrafiltration or ultracentrifugation.
- 30. The separation of crystalloids from colloids by diffusion through parchment/animal membrane is called dialysis.
- 31. Ultra filters are prepared by treating filter paper with colloidion or gelation solution followed by hardening with formaldehyde.
- 32. In ultracentrifugation, the colloidal sol is taken in a tube rotated at high speed in ultracentrifuge. Colloidal particles settle down, which are separated and mixed with the dispersion medium.

- 33. Coagulation occurs (a) by addition of electrolyte, (b) by electrophoresis, (c) by mixing oppositely charged sols, (d) by prolonged dialysis, and (e) by heating or cooling.
- 34. Emulsions are colloidal systems in which both dispersed phase and dispersion medium are liquids. These can be of (a) oil-in-water type and (b) water-in-oil type.
- 35. The process of making emulsion is called *emulsification*.
- 36. To stabilize an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used as emulsifiers.
- 37. The most common emulsifiers are soaps.
- 38. Milk is an emulsion of oil in water (fats in water) while cod liver oil is water in oil.
- 39. Presence of soluble soaps as emulsifying agent gives oil-inwater type emulsion while that of insoluble soaps results in water-in-oil type emulsion.
- 40. If on adding an electrolyte to an emulsion, conductance increases, it is oil-in-water type.
- 41. Latex is colloidal dispersion of rubber particles in water.
- 42. The swelling of gel when placed in water is called imbibition.
- 43. Some gels on shaking change into liquid which on standing again changes into gel. This property is called thixotropy.
- 44. A catalyst is a substance which can change the speed of a chemical reaction without being used up in the reaction. If it increases the speed of the reaction, it is called positive catalyst and if it decreases the speed of the reaction. It is called negative catalyst. Further, if the catalyst and the reactants are present in the same phase, it is called homogeneous catalysis but if they are in different phase, it is called heterogeneous catalysis. Homogeneous catalysis is explained by intermediate compound formation theory while heterogeneous catalysis is explained by adsorption theory.
- 45. Zeolites are aluminosilicates. They form an important class of oxide catalysts. On heating in vacuum they lose water of hydration and become porous. They are used as shapeselective catalysts.
- 46. Enzymes are biological catalysts. They are globular proteins some of which contain a non-protein component called cofactor for their activity. Their main characteristics are their specificity, efficiency (even in small amounts) and activity at physiological temperature of 37°C and pH of 7.4. Their action is explained by lock and key model or by hand and glove model (also called induced-fit model).
- 47. Enzyme-catalyzed reaction takes place in two steps as:
 - **a.** $E + S \rightleftharpoons ES$ (fast and reversible)
 - **b.** ES \longrightarrow E + P (slow and rate determining)
 - (E is enzyme, S is substrate, and P is product)
- 48. Auto catalysis: In certain reactions, one of the products acts as a catalyst. In the initial stage, the reaction is slow but as soon as the product comes into existence, the reaction rate increases.
- 49. Induced catalysis: When one reaction influences the rate of another reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.
- 50. Promoters are those substances which when added in small amount with the catalysts enhance the efficiency of catalyst.
- 51. Poisons are the substances which destroy the activity of the catalyst by their presence.

5,1 INTRODUCTION

of the chemistry deals with the phenomenon that occurs at the interfaces. There are several property of interfaces. There are several properties of substances, aufface of solids and liquids and solids and gases, which depend the nature of the surface or interface. An interface or surface surrace of surface of skill. For example, the interface between a solid and a gas may represented by solid-gas or solid/gas. The bulk phases that we onsider in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends athesize of the particle of bulk phase. Many important phenomena, ath as electrode processes, heterogeneous catalysis, corrosion, aborption on solid or on solution surface, colloidal properties, etc., important surface effects which are useful to understand many and chemical properties of the substances.

The subject of surface chemistry has many applications in analytical work, and daily life situations. In this chapter, we all be studying some important features of surface chemistry such sadsorption, catalysis, and colloids including emulsions and gels.

5.2 ADSORPTION

Adsorption is essentially a surface phenomenon. There are several examples which reveal that the surface of a solid has the tendency n attract and retain the molecules of the phase with which it comes mic contact. These molecules remain only at the surface and do m penetrate deeper into the bulk. For example, when a small amount of finely divided charcoal is put into a vessel containing agas, it is observed that the pressure of the gas first rapidly and and gradually decreases. The decrease in pressure of the gas is to the accumulation of gas on the surface of charcoal. Figure shows adsorption of a gas at the solid surface.

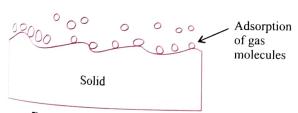


Fig. 5.1 Adsorption of a gas at the solid surface

The phenomenon of attracting and retaining the molecules substance on the surface rather than in the bulk of a solid or and resulting into higher concentration of the molecules on the Mace is termed adsorption.

The molecular species or substance which concentrates or in molecular species or substance which community at the surface is termed adsorbate and the material on the which adsorption takes place is called adsorbent (Fig. 5.2).

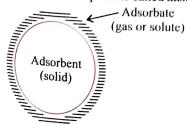


Fig. 5.2 Adsorbent and adsorbate

The adsorbent may be solid or a liquid and the adsorbate may be a gas or a solute in some solution.

The adsorption of gases on metal surfaces is called occlusion. A few examples of adsorption are as follows:

- a. If a gas such as O₂, H₂, Cl₂, NH₃, or SO₂ is taken in a closed vessel containing powdered charcoal, its molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface. Solids, particularly in a finely divided state, have large surface area and therefore charcoal, silica gel, alumina gel, clay, colloids, and metals in finely divided state act as good adsorbents.
- b. In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.
- c. Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
- d. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

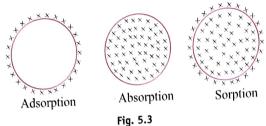
It is clear from the above examples that solid surface can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.

5.2.1 DISTINCTION BETWEEN ADSORPTION AND ABSORPTION

Adsorption is a phenomenon in which a substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent. On the other hand, absorption is a phenomenon in which the molecules of a substance are uniformally distributed throughout the bulk of the solid.

For example, when a chalk stick is dipped in ink the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption, the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.

Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes. Figure 5.3 illustrates adsorption, absorption, and sorption.



The important points of difference between adsorption and absorption are listed in Table 5.1.

Table 5.1 Differences between adsorption and absorption

Adsorption	Absorption
 a. It is a surface phenomenon i.e., it occurs only at the surface of the adsorbent. b. In this phenomenon, the concentration on the surface of adsorbent is different from that in the bulk. c. Its rate is high in the beginning and then decreases till equilibrium is attained. 	 a. It is a bulk phenomenon, i.e., it occurs throughout the body of the material. b. In this phenomenon, the concentration is same throughout the material. c. Its rate remains same throughout the process.

Positive adsorption: When the concentration of the adsorbate is more on the surface of adsorbent relative to its concentration in the bulk, it is called positive adsorption.

Negative adsorption: When the concentration of the adsorbate is less on the surface relative to its concentration in the bulk, it is called negative adsorption. For example, in the case of some liquid solutions, it is observed that the concentration of the solute is less on the surface than in the bulk of the solution. This type of adsorption is called negative adsorption.

5.2.2 MECHANISM OF ADSORPTION

Adsorption arises because of the unbalanced forces on the surface of the adsorbent (Fig. 5.4). If we consider a solid, it is observed that a molecule present in the bulk of the solid is being uniformally attracted form all sides by the neighbouring molecules. As a result, there is no net pull on this molecule. However, a molecule which lies near the surface is being attracted only by molecules below it. Therefore, surface molecules experience a resultant downward attractive force within the solid. In other words, the surface is under strain or tension due to unbalanced forces. As a result, the surface of the solid tends to satisfy its residual forces by attracting and retaining the molecules of the adsorbate when brought in contact with them. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure. This shows that with the increase of surface area, the unbalanced attractive forces of the surface are also increased.

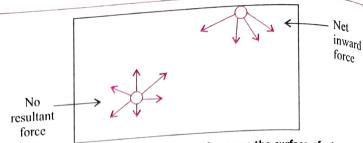


Fig. 5.4 Adsorption due to unbalanced forces on the surface of adsorbent

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in the residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to a decrease in the entropy of the gas after adsorption, i.e., ΔS is negative Adsorption is thus accompanied by a decrease in the enthalpy as well as a decrease in the entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e. there is a decrease in Gibbs energy. On the basis of equation. $\Delta G = \Delta H - T \Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process. which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative, ultimately ΔH becomes equal to $T \Delta S$ and ΔG becomes zero. At this state equilibrium is attained and hence it is called adsorption equilibrium.

5.2.3 Types of Adsorption

Adsorption of gases on solid is mainly classified into two types. depending upon the nature of forces which hold the molecules of the adsorbate on the surface of the adsorbent.

- a. Physical adsorption or physisorption
- b. Chemical adsorption or chemisorption
- a. Physical adsorption: If the particles of an adsorbate are held to the surface of the adsorbent by the physical forces such as van der Waals forces, the adsorption is termed as physical adsorption or physisorption. The attractive forces are weak, and therefore, these can be easily overcome either by increasing the temperature or by decreasing the pressure. In other words, physical adsorption can be easily reversed Following are the characteristics of physisorption:
 - Lack of specificity: A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals forces are universal.
 - ii. Nature of adsorbate: The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals forces are stronger near the critical temperatures. Thus, l g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630 K) than methane (critical

temperature 190 K) which is still more than 4.5 mL temperature 33 K).

Reversible nature: Physical adsorption of a gas by a solid is generally reversible. Thus,

Solid + Gas Gas/Solid + Heat

More of gas is adsorbed when pressure is increases More volume of the gas decreases (Le-Chatelier's as the chatter's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low time Physical decreases with increasing temperature temperature (Le-Chatelier's principle).

- iv. Surface area of adsorbent: The extent of adsorption increases with an increase of the surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.
- Enthalpy of adsorption: No doubt, physical adsorption is an exothermic process, but its enthalpy of adsorption is quite low (20–40 kJ mol⁻¹). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals forces.
- h. Chemical adsorption: When the molecules of the adsorbate are held to the surface of the adsorbent by the chemical bonds, the adsorption is termed as chemical adsorption or chemisorption. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. This type of adsorption is irreversible.

Following are the characteristics of chemisorption:

- i. High specificity: Chemisorption is highly specific and will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.
- ii. Irreversibility: As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.
- iii. Surface area: Like physical adsorption chemi-sorption also increases with increase of surface area of the adsorbent.
- iv. Enthalpy of adsorption: The enthalpy of chemisorption is high $(80-240 \text{ kJ mol}^{-1})$ as it involves chemical bond formation.

Difference between physical adsorption and chemical

The main differences between physical adsorption and chemical adsorption are summed up in Table 5.2.

Table 5.2 Diffe

able 5.2 Difference between phys	sisorption and chemisorption
	Chemisorption
 Physisorption a. The forces operating in these cases are weak van der Waals forces. b. The heat of adsorption is low, viz., about 20–40 kJ mol⁻¹. c. No compound formation takes place in these cases d. The process is reversible, i.e., desorption of the gas occurs by increasing the temperature or decreasing the pressure. e. This type of adsorption decreases with increase of temperature. 	 a. The forces operating in these cases are similar to those of a chemical bond. b. The heat of adsorption is high, viz., about 80–240 kJ mol⁻¹. c. Surface compounds are formed. d. The process is irreversible. Efforts to free the adsorbed gas give some definite compound. e. This type of adsorption first increases with increase of temperature and then decreases. The effect is called activated
P = Constant $t \longrightarrow$ Physisorption isobar f. It is not specific in nature i.e., all gases are adsorbed on all solids to some extent.	adsorption. $P = Constant$ Chemisorption isobar f. It is specific in nature and occurs only when there is some possibility of compound formation between the gas being adsorbed and the solid adsorbent.
g. The amount of the gas adsorbed is related to the ease of liquefication of the gas.h. It forms multimolecular lay	
i. The rate of adsorption increases with increase in pressure of adsorbate.	 i. The rate of adsorption usually decreases as the pressure increases.

5.2.4 FACTORS AFFECTING ADSORPTION OF GASES ON SOLIDS

The extent of adsorption of a gas on a solid surface is affected by the following factors:

- a. Nature of gas
- b. Nature and specific area of adsorbent
- c. Effect of pressure
- d. Effect of temperature
- e. Activation of absorbent

Nature of the Gas

Different gases are adsorbed to different extents by the same adsorbent at same temperature. The physical adsorption is nonspecific in nature and therefore every gas gets adsorbed on the surface of any solid to a lesser or greater extent. However, under given conditions of temperature and pressure, the easily liquefable gases such as CO2, HCl, and NH3 are adsorbed more than the permanent gases such as H₂, N₂, or O₂. This is illustrated in Table 5.3 in which the volumes of different gases (reduced to NTP conditions) adsorbed by 1 g of charcoal at 288 K have been given. The critical temperatures of the gases are also included in Table 5.3.

Table 5.3 Volume of gases at NTP adsorbed by 1 g of charcoal

at 2	1	N.	CO	CH_{4}	CO,	HCl	NH_3	SO_2
Gas	H_2	- 2		7	48	72	181	380
Volume adsorbed (cc)	4.7	8.0	9.3	16.2			7	4 3 0
Critical temperature (K)	33	126	134	190	304	324	406	

From the table, it may be seen that higher the critical temperature of a gas, greater is the amount of that gas adsorbed. In other words, a gas which is more easily liquefiable or is more soluble in water is more readily adsorbed. This relationship is not surprising as the critical temperature of a gas is related to the intermolecular forces which is an important factor for adsorption too.

Nature and Specific Area of Adsorbent

The extent of adsorption of a gas depends upon the nature of adsorbent. Most common adsorbents are activated charcoal, finely divided metals, and metal oxides (silica gel, aluminium oxide, etc.). Each of these have their own adsorption properties. The larger the surface area of the solid, the greater would be its absorbing capacity. Therefore, the porous and finely divided forms of adsorbents absorb large quantities of adsorbate.

Effect of Pressure

The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas. The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm. The extent of adsorption is usually expressed as x/m where x is the mass of adsorbate and m is the mass of the adsorbent. The adsorption isotherm is shown in Fig. 5.5.

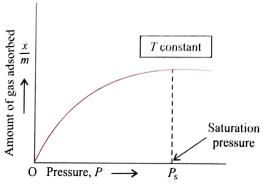


Fig. 5.5 Adsorption isotherm

It is clear from the figure that the extent of adsorption (x/m)increases with pressure and reaches maximum, corresponding to pressure P_s , called equilibrium pressure. Since adsorption is a pressure 1 s, cance of the state of the stat reversible process, described becomes equal to the this pressure (P_s) , the amount of gas adsorbed becomes equal to the amount of gas desorbed so that the extent of adsorption becomes constant even though the pressure is increased. This state is also called saturation state and P_s is called saturation pressure.

Adsorption isotherm: Scientists have explained adsorption in terms of some empirical mathematical relations called adsorption isotherm. The most common types are:

a. Freundlich adsorption isotherm: In 1909, Freundlich gave a mathematical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed as:

$$\frac{x}{m} = KP^{1/n} \ (n > 1) \dots (i)$$

where x is the mass of gas
adsorbed on mass m of the
adsorbent at pressure P; K
and n are constants which
depend on the nature of the
adsorbent and the gas at
a particular temperature.
The relationship is gener-
ally represented in form

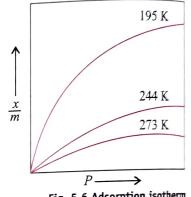


Fig. 5.6 Adsorption isotherm

of a curve where the mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.6). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with an increase in temperature. These curves always seem to approach saturation at high pressure.

Calculation of K and n of adsorption isotherm Taking logarithm of Eq. (i),

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P \qquad ...(ii)$$

The validity of Freundlich isotherm can be verified by plotting $\log (x/m)$ on y-axis (ordinate) and $\log P$ on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.7). The slope of the straight line gives the value of 1/n. The intercept on the y-axis gives the value of log K.

Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor 1/n can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, Eq. (ii) holds good over a limited range of pressure.

From the Freundlich isotherm, the following observation can be easily observed (Fig. 5.7):

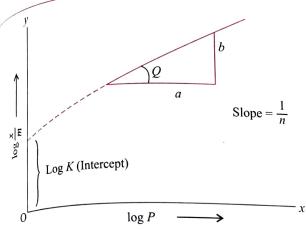


Fig. 5.7 Freundlich isotherm

i. At low pressure: When $\frac{1}{n} = 1$, $\frac{x}{m} = KP$, i.e., $x/m \propto P$ which means that x/m is directly proportional to the pressure. The graph is almost straight line. It follows first-order kinetics.

ii. At high pressure: When $\frac{1}{n} = 0$, $\frac{x}{m} = \text{constant}$, which means that adsorption is independent of pressure. The graph becomes almost constant. This can be expanded as:

$$\frac{x}{m} = KP^{1/n}$$

$$\Rightarrow \frac{x}{m} = KP^{0} \qquad \left(\frac{1}{n} = 0\right)$$

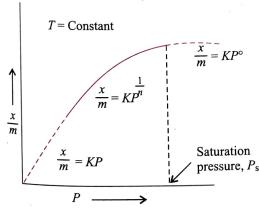
$$= K \qquad (P^{0} = 1)$$

It follows zero-order kinetics.

iii. At intermediate range of pressure: At intermediate range of pressure x/m will depend upon the power of pressure which lies between 0 and 1. This can be expressed as:

$$\frac{x}{m} = KP^{1/n}$$

where n can take any whole number.



Variation of x/m with increase in pressure at constant temperature (general adsorption isotherm)

b. Langmuir adsorption isotherm: One of the drawbacks of the Freundlich adsorption isotherm is that it fails at high pressure of the gas. Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases. This is named as the Langmuir adsorption

isotherm. This isotherm is based on the assumption that every adsorption site is equivalent and that the ability of particle to bind there is independent of whether or not nearby sites are occupied. In his derivation, Langmuir considered adsorption to consist of following two opposing processes:

- i. Adsorption of gas molecules on the surface of the solid.
- **ii.** Desorption of adsorbed molecules form the surface of the solid.

Langmuir believed that eventually a dynamic equilibrium is established between the above two opposing processes. He also assumed that the layer of the adsorbed gas was only one molecule thick, i.e., unimoleuclar. Since such type of adsorption is obtained in the case of chemisorption, Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation:

$$\frac{x}{m} = \frac{aP}{1 + bP} \qquad \dots (i)$$

where a and b are two Langmuir parameters. At very high pressure, the above isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{P}$$
 (at very high pressure) ...(ii)

At very low pressure, Eq. (i) is reduced to

$$x/m = aP$$
 (at very low pressure) ...(iii)

In order to determine the parameters a and b, Eq. (i) may be written in its inverse form:

$$\frac{m}{x} = \frac{1+bP}{aP} = \frac{b}{a} + \frac{1}{aP} \qquad \dots (iv)$$

A plot of m/x against 1/P gives a straight line with slope and intercept equal to 1/a and b/a, respectively. Thus, both parameters can be determined.

The Langmuir isotherm, in the form of Eq. (i) is generally more successful in interpreting the data than the Freundlich isotherm when a monolayer or a unimolecular adsorbed layer is formed. A plot of x/m versus P is shown in Fig. 5.9.

At low pressures, according to Eq. (iii), x/m increases linearly with P. At high pressure, according to Eq. (ii), x/m becomes constant, i.e., the surface is fully covered and change in pressure has no effect and no further adsorption takes place, as is evident from Fig. 5.9.

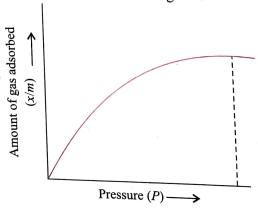


Fig. 5.9

Effect of Temperature

Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic, therefore, the reverse process, i.e., desorption, is endothermic. If the above equilibrium is subjected to change in temperature, then according to Le-Chatelier's principle, with decrease in temperature adsorption will increase and vice-versa. Thus, with the increase in temperature at constant pressure, the extent of adsorption (x/m) will decrease. However, this is true only for physical adsorption as shown in Fig. 5.10(a). In case of chemisorption, the adsorption initially increases with rise in temperature and then decreases as shown in Fig. 5.10(b).

This behaviour is expected because, like all chemical reactions, some activation energy is required for chemisorption. At low temperature, x/m is small. As temperature is increased, the molecules of the adsorbate gain energy and become equal to activation energy so that proper bonds are formed with the adsorbent molecules. Therefore, initially, the amount of gas adsorbed increases with rise in temperature. Further increase of temperature will increase the energy of molecules which have already been adsorbed. This would increase the rate of desorption and, therefore, decrease the extent of adsorption.

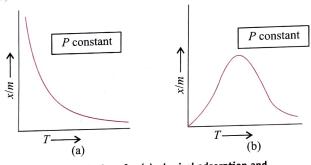


Fig. 5.10 Adsorption isobars for (a) physical adsorption and (b) chemical adsorption

The graph between the extent of adsorption and temp-erature at constant pressure is called adsorption isobar.

Activation of the Solid Adsorbent

Activation of the solid adsorbent means increasing the adsorbing power of an adsorbent. This is usually done by increasing the surface area (or the specific area) of the adsorbent which can be achieved in any of the following ways:

- a. By making the surface of the adsorbent rough, e.g., by mechanical rubbing or by chemical action or by depositing finely dispersed metals on the surface of the adsorbent by electroplating.
- b. By subdividing the adsorbent into smaller pieces or grains. No doubt this method increases the surface area but it has a practical limitation, that is, if the adsorbent is broken into very fine particles that it becomes almost powder, then the penetration of the gas becomes difficult and this obstructs adsorption.
- c. By removing the gases already adsorbed, e.g., charcoal is activated by heating in superheated steam or in vacuum at a temperature between 623 and 1273 K.

5.2.5 ADSORPTION FROM SOLUTION PHASE

The process of adsorption can take place from solutions also. It is observed that solid adsorbents adsorb certain solutes from solution in preference to other solutes and solvents. For example, animal charcoal decolourizes impure sugar by adsorbing colouring dye in preference to sugar molecules.

Similarly, the litmus solution when shaken with charocal becomes colourless. The precipitate of Mg(OH)₂ attains blue colour when precipitated in presence of Magneson reagent. The colour is due to adsorption of magneson. The following observation have been made in the case of adsorption from solution phase:

- a. The extent of adsorption decreases with an increase in temperature.
- b. The extent of adsorption increases with an increase of surface area of the adsorbent.
- c. The extent of adsorption depends on the concentration of the solute in solution.
- d. The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

Freundlich adsorption and Langmuir adsorption isotherms have been found to be applicable in the adsorptions from solutions. Temperature dependence here also is similar to that for the adsorption of gases. However, in place of equilibrium pressure, we use equilibrium concentrations of the adsorbates in the solution and the isotherms take the form

$$\frac{x}{m} = Kc^{1/n} \tag{i}$$

Taking logarithms, Eq. (i) becomes

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log c$$

A graph between x/m and c has been found to be similar to one shown for x/m and P for gases on solid (Fig. 5.8).

From the graph, the values of 1/n and $\log K$ can be calculated as slope and intercept, respectively.

Similarly, Langmuir adsorption isotherm may be written as:

$$\frac{x}{m} = \frac{ac}{1 + bc}$$

The parameters of above equations can be determined by the method described earlier for adsorption of gases on solids.

5.2.6 APPLICATION OF ADSORPTION

The phenomenon of adsorption finds a number of applications. Important ones are listed below:

- a. Production of high vacuum: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.
- b. In curing disease: A number of drugs are used to kill germs by getting adsorbed on them.
- c. Froth floatation process: A low-grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.
- d. Adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes such as eosin, fluorescein, etc., and thereby producing a characteristic colour at the end point.

In ion-exchange resin: The organic polymers containing in ion-exchange resin: The organic polymers containing in ion-exchange resin: The organic polymers containing groups such as -COOH, -SO₃H, and -NH₂, etc., possess the property of selective adsorption of ions from solutions. These are quite useful in the softening of water.

Surfactants: Surfactants work as emulsifiers in the manufacture of emulsion. Emulsifiers work on the principle of adsorption.

Gas masks: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

Control of humidity: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

Removal of colouring matter from solutions: Animal charcoal removes colours of solutions by adsorbing coloured impurities.

Heterogeneous catalysis: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. The manufacture of ammonia using iron as a catalyst, the manufacture of H₂SO₄ by contact process, and the use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

L Separation of inert gases: Due to the difference in the degree of adsorption of gases by charcoal, mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

LLUSTRATION 5.1

What is physical adsorption?

If the adsorbate is held on a surface by weak van der Waals forces, the adsorption is called physical adsorption.

LLUSTRATION 5.2

What is sorption?

Sorption is the process in which adsorption and absorption take place simultaneously, e.g., dyeing of cotton fibres by azo dyes.

LLUSTRATION 5.3

Why are powdered substances more effective adsorbent than their crystalline forms?

Powdered substances have greater surface area as compared to their crystalline forms. Greater the surface area, greater is the adsorption.

LLUSTRATION 5.4

How do size of particles of adsorbent, pressure of gas, and prevailing temperature influence the extent of adsorption of a gas on a solid?

Sol.

a. Smaller the size of the particles of an adsorbent, greater is the surface area and greater is the adsorption.

b. At constant temperature, adsorption first increases with increase of pressure and then attains equilibrium at high pressures.

c. In physical adsorption, it decreases with increase of temperature but in chemisorption, first it increases and then decreases.

ILLUSTRATION 5.5

Why physisorption is multi-molecular whereas chemisorption is unimolecular?

Sol. Chemisorption takes place as a result of the reaction between adsorbent and adsorbate. When the surface of the adsorbent is covered with one layer, no further reaction can take place. Physisorption is simply by van der Waals forces. So any number of layers may be formed one over the other on the surface of the adsorbent.

ILLUSTRATION 5.6

Compare the heat of adsorption for physical and chemical adsorption?

Sol. The heat of adsorption for chemical adsorption is high (of the order of 80–400 kJ mol⁻¹) while the heat of adsorption for physical adsorption is low (of the order of 20–40 kJ mol⁻¹).

ILLUSTRATION 5.7

In the case of chemisorption, why adsorption first increases and then decreases with temperature?

Sol. Chemisorption involves activation energy. The initial increase in chemisorption is due to the fact that the heat supplied acts as activation energy and more and more molecules of adsorbate gain energy and possess energy greater than activation energy. Therefore, adsorption increases with increase in temperature. Further increase will increase the energy of the molecules absorbed and will also increase the rate of desorption. Therefore, the extent of adsorption decreases.

ILLUSTRATION 5.8

Which will be adsorbed more readily on the surface of charcoal and why—NH₃ or CO₂?

Sol. NH₃ has higher critical temperature than CO₂, i.e., NH₃ is more liquefiable than CO₂. Hence, NH₃ has greater intermolecular forces of attraction and hence will be adsorbed more readily.

ILLUSTRATION 5.9

Give the expression of Freundlich isotherms.

Sol.
$$\frac{x}{m} = KP^{1/n}$$
 or $\log \frac{x}{m} = \log K + \frac{1}{n} \log P$

where m is the mass of the adsorbent and x that of adsorbate, P is the pressure of the gas, and n is an integer.

ILLUSTRATION 5.10

What is meant by chemical adsorption?

Sol. If the adsorbate is held on the surface of the adsorbent as a result of chemical reaction forming surface compounds, it is called chemical adsorption.

ILLUSTRATION 5.11

What is desorption?

Sol. The process of removal of adsorbed substance is called desorption.

ILLUSTRATION 5.12

What is occlusion?

Sol. The adsorption of gases on the surface of metals is called occlusion.

ILLUSTRATION 5.13

Explain the following observations.

- a. Sun looks red at the time of sunset.
- **b.** Rate of physical adsorption decreases with rise in temperature.
- c. Physical adsorption is multilayered while chemical adsorption is monolayered.

Sol.

- a. At the time of sunset, the sun is at horizon. The light emitted by the sun has to travel a relatively longer distance through the atmosphere. As a result, blue part of light is scattered away by the particulate in the atmosphere causing red part to be visible.
- **b.** Gas (adsorbate) + Solid (adsorbent)

Physical adsorption is an exothermic process. At equilibrium as the temperature is increased, by Le-Chaterlier's principle, the equilibrium shifts in the backward direction, i.e., adsorption decreases.

c. Physical adsorption involves van der Waals forces, so any number of layers may be formed one over the other on the surface of the adsorbent. Chemical adsorption takes place as a result of the reaction between adsorbent and adsorbate. When the surface of adsorbent is covered with one layer, no further reaction can take place.

ILLUSTRATION 5.14

How is adsorption of a gas related to its critical temperature?

Sol. Higher the critical temperature of a gas, greater the ease of liquefication, i.e., greater the van der Waals forces of attraction and hence greater the adsorption.

ILLUSTRATION 5.15

List four applications of adsorption.

Sol.

- a. Heterogeneous catalysis is based on the adsorption of gases on solid.
- b. Chromatograph is based on differential adsorption.
- c. Charge on colloidal solution is due to selective adsorption of common ions on the surface.
- d. Carbon particles from smoke get adsorbed on the surface of electrodes of cotterell smoke precipitators.

ILLUSTRATION 5.16

In an experiment, 200 mL of 0.5 M oxalic acid is shaken with 10 g of activated charcoal and filtered. The concentration of the filtrate is reduced to 0.4 M. The amount of adsorption (x/m) is

- a. 0.9
- **b.** 1.8
- c. 0.180
- d. 0.09

Sol.

c. Mass of oxalic acid adsorbed by 10 g charcoal $= 200 \times 10^{-3} (0.5 - 0.4) \times 90 = 1.8 \text{ g}$ (Mw or oxalic acid = 90 g mol⁻¹)

The amount of adsorption

$$\frac{x}{m} = \frac{1.8}{10} = 0.18$$

ILLUSTRATION 5.17

 $2.0\,\mathrm{g}$ of charcoal is placed in $100\,\mathrm{mL}$ of $0.05\,\mathrm{M}$ CH₃COOH to form an adsorbed mono-acidic layer of acetic acid molecules and thereby the molarity of CH₃COOH reduces to 0.49. The surface area of charcoal is $3\times10^2\,\mathrm{m}^2\,\mathrm{g}^{-1}$. The surface area of charcoal adsorbed by each molecule of acetic acid is

a.
$$1.0 \times 10^{-18} \text{ m}^2$$

b.
$$1.0 \times 10^{-19} \text{ m}^2$$

c.
$$1.0 \times 10^{13} \text{ m}^2$$

d.
$$1.0 \times 10^{-22}$$
 m

Sol.

a. CH_3COOH adsorbed = 0.5 - 0.49 = 0.01 M

Number of molecules adsorbed =
$$0.01 \times \frac{100}{1000} \times 6$$

 $\times 10^{23} = 6 \times 10^{2}$

Total area of charcoal =
$$2 \times 3 \times 10^2 = 600 \text{ m}^2$$

$$\Rightarrow$$
 Area per molecule = $\frac{600}{6 \times 10^{20}} = 1 \times 10^{-18} \text{ m}^2$

ILLUSTRATION 5.18

Which of the following statements is not true?

- a. Both physisorption and chemisorption are exothermic.
- **b.** Physisorption takes place with decrease of free energy whereas chemisorption occurs with increase of free energy.
- c. Physisorption requires low activation energy but chemisorption requires high activation energy.
- **d.** The magnitude of chemisorption increases and that of physisorption decreases with rise in temperature.

b. For physisorption and chemisorption free energy change (ΔG) is negative.

LUSTRATION 5.19

The fale of chemisorption The law increases with decrease in temperature

increases with increase in temperature

increases with decrease in the pressure of gas

is independent of the pressure of gas

h. Chemisorption involves high activation energy and increases to a maximum value with rise in temperature.

LUSTRATION 5.20

Which of the two, He and Ne, gets adsorbed on the surface of charcoal more readily and why?

Ne will get adsorbed to more extent because it has large surface area, therefore, more van der Waals forces of attraction. Also it is more easily liquifiable as compared to He. More easily liquefiable gases are adsorbed to a greater extent.

LUSTRATION 5.21

Adsorption, if spontaneous, is exothermic. Explain.

Adsorption is accompanied by decrease in entropy, i.e., ΔS = -ve. If it is spontaneous than ΔG should be negative $\Delta G = \Delta H - T \Delta S.$

Since ΔS is -ve (entropy decreases in the process of adsorption), ΔG will be negative, only if $\Delta H = -\text{ve}$, i.e., if the process is exothermic.

CONCEPT APPLICATION EXERCISE 5.1

- 1. Explain the following terms
 - c. Adsorbent b. Adsorbate a. Adsorption
- 2. Discuss the effect of pressure and temperature on the adsorption of gases by solids.
- 3. How is the adsorption of a gas related to its critical temperature?
- 4. Derive the following:
 - b. Freundlich isotherm a. Langmuir isotherm
- 5. Write differences between physisorption and chemisorption.
- 6. Which of the two, adsorption or absorption, is surface phenomenon?
- 7. Why finely divided substance is more effective as an adsorbent?
- 8. Discuss different types of adsorption and their properties.

5.3 CATALYSIS

The substances which alter the velocity of a reaction and themselves remain chemically and quantitatively unchanged after the reaction; are known as catalysts, and the phenomenon is known as catalysis.

Catalysts are not consumed in the reaction, hence very small non-stoichiometric quantities are generally required. For example, when potassium chlorate heated strongly decomposes slowly giving dioxygen, the decomposition occurs in the temperature range of 653-873 K.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633 K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. Thus, manganese dioxide acts as a catalyst for the above reaction.

5.3.1 PROMOTERS AND POISONS

Promoters are substances that, if present along with a catalyst, enhances the activity of a catalyst. For example, in Haber's process, for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

Poisons are substances that decrease the activity of a catalyst. These substances are called catalytic poisons. For example:

- a. The activity of iron catalyst is destroyed by the presence of H₂S or CO in the synthesis of ammonia by Haber's process.
- b. The presence of traces of arsenious oxide (As₂O₃) in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

5.3.2 TYPES OF CATALYSIS

Based on the type of catalytic reactions, catalysis is of following types:

- a. Positive catalysis: If a catalyst increases (accelerates) the rate of a reaction, it is called a positive catalyst and the phenomenon is called positive catalysis.
 - Positive catalyst increases the rate by lowering the activation energy of reaction. A catalyst provides an entirely new path for the reaction in which a newly activated intermediate complex of lower potential energy is formed.

This means that the catalyst provides a new pathway of lower activation energy. Consequently, the fraction of the total number of collisions possessing lower activation energy is increased and hence the rate of reaction also increases. Figure 5.11 gives an energy diagram which depicts the effect of a catalyst on the activation energy. The solid line shows the path for uncatalyzed reaction and the dotted line shows the path adopted by catalyzed reaction.

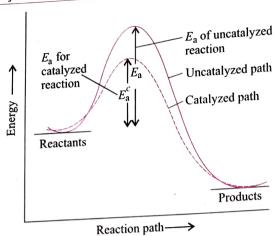


Fig. 5.11 Comparison of activation energies of a catalyzed and an uncatalyzed

Some examples of positive catalysis are as follows:

i. Decomposition of H₂O₂ in the presence of colloidal platinum

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

ii. Hydrogenation of vegetable oil in the presence of nickel

Vegetable oil(1) +
$$H_2(g) \xrightarrow{Ni(s)}$$
 Ghee(s)

iii. Formation of methane in the presence of nickel

$$CO(g) + 3H_2(g) \xrightarrow{Ni(s)} CH_4(g) + H_2O(g)$$

iv. Oxidation of sulphur dioxide in the presence of nitric oxide

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

- **b.** Negative catalysis: If a catalyst decreases (retards) the rate of a reaction, it is called negative catalyst and the phenomenon is called negative catalysis. For example:
 - Addition of small amount of acetanilide shows slow decomposition of hydrogen peroxide.
 - ii. Tetraethyl lead (TEL) acts as an antiknocking agent in the case of petrol. Thus, it decreases the knocking of petrol and acts as a negative catalyst.
 - **iii.** The oxidation of sodium sulphite by air is retarded by alcohol.

$$2\text{Na}_2\text{SO}_3(s) + \text{O}_2(g) \xrightarrow{\text{Alcohol(l)}} 2\text{Na}_2\text{SO}_4(s)$$

iv. The oxidation of chloroform by air is retarded if some alcohol is added.

$$2 \text{CHCl}_3(l) + \text{O}_2(g) \xrightarrow{\text{Alcohol(l)}}$$

$$2 \text{COCl}_2(g) + 2 \text{HCl}(g)$$

c. Auto-catalysis: In certain reactions, one of the products acts as a catalyst. In the initial stage the reaction is slow but as soon as products are formed, one of the products itself acts as a catalyst, and hence the reaction is known as autocatalysis. For example:

- i. When nitric acid is poured on copper, the reaction is very slow in the beginning. Gradually, the reaction becomes faster due to formation of nitrous acid during the reaction which acts as an auto-catalyst.
- ii. In the hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to the formation of acetic acid which acts as an auto-catalyst in this reaction.

reaction.
$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

- d. Induced catalysis: When one reaction influences the rate of other reaction, which does not occur under ordinary conditions the phenomenon is known as induced catalysis. Some examples are as follows:
 - i. Reduction of mercuric chloride (HgCl₂) with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and mercuric chloride, both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.
 - ii. Sodium arsenite solution is not oxidized by air, if, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

Depending on whether a catalyst is in the same phase as the reaction mixture, catalysis is divided into two types:

a. Homogeneous catalysis: If a catalyst is present in the same phase as the reactants, it is called a homogeneous catalyst and this type of catalysis is called homogeneous catalysis. It is believed that in homogeneous catalysis, a catalyst enters into chemical combination with one or more of the reactants forming an intermediate compound which then decomposes or combines with one of the reactants to produce the product and the catalyst is regenerated.

A thoroughly studied example of homogeneous catalysis is the hydrolysis of organic ester (RCOOR').

Here R and R' are alkyl groups, R-C-OH is a carboxylic acid and R-OH is an alcohol. The reaction rate is low at room temperature but can be increased by adding a small amount of a strong inorganic acid which provides H^{\oplus} ions that acts as a catalyst in the reaction. Some other examples of homogeneous catalysis are:

i. Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

ii. Hydrolysis of methyl acetate is catalyzed by H^{\oplus} ions furnished by hydrochloric acid

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCI(l)} CH_3COOH(aq) + CH_3OH(aq)$$

Both the reactants and catalyst are in the same phase.

iii. Hydrolysis of sugar is catalyzed by H[®] ions furnished by sulphuric acid

$$C_{12}H_{22}O_{11}(aq) + H_2O(1) \xrightarrow{H_2SO_4(1)} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$
Glucose Fructose

iv. Catalytic decomposition of ozone by chlorine atoms in the gas phase

$$O_3(g) + O(g) \xrightarrow{Cl(g)} 2O_2$$

- v. Oxidation of CO by O_2 in the presence of NO as catalyst $2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$
- b. Heterogeneous catalysis: When the catalyst is in different phase than the reactants, it is called heterogeneous catalyst, and this type of process is called heterogeneous catalysis.

In heterogeneous catalysis, the catalyst is generally a solid and the reactants are generally gases, but sometimes liquid reactants are also used. It is also known as surface catalysis, as the reaction starts at the surface of the solid catalyst. These catalysts have enormous surface areas between 1 and $500 \, \text{m}^2 \, \text{g}^{-1}$ for contact. Interestingly, many reactions that occur on a metal surface such as the decomposition of HI on gold and the decomposition of N_2O on platinum are zero order because the rate-determining step occurs on the surface itself. Thus, despite an enormous surface area, once the reactant gas covers the surface, it increases the rate of reaction.

One of the most important examples of heterogeneous catalysis is the addition of H_2 to the C=C bonds of organic compounds to form C—C bonds. This is known as catalytic hydrogenation reaction. The petroleum, plastics and food industries frequently use catalytic hydrogenation.

Examples of heterogeneous catalysis are given below:

 i. Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt

$$2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

The reactant is in gaseous state while the catalyst is in the solid state.

 ii. Combination between dinitrogen and dihydrogen to form ammonia in the presence of finely divided iron in Haber's process

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

iii. Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

The reactants are in gaseous state while the catalyst is in the solid state.

iv. Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst

Vegetable oils(1) + $H_2(g) \xrightarrow{Ni(s)}$ Vegetable ghee(s) One of the reactants is in liquid state and the other in gaseous state while the catalyst is in the solid state.

Catalytic converter for an automobile

The catalytic converter in the car's exhaust which converts polluting exhaust gases into non-toxic ones contains a heterogeneous catalyst. In a single pass through the catalyst bed, CO and unburned petrol are oxidized to CO_2 and $\mathrm{H}_2\mathrm{O}$, while NO is reduce to N_2 . Mixtures of transition metals and their oxides embedded in inert supports act as a catalyst.

$$2CO + O_2 \xrightarrow{Catalyst} 2CO_2$$

$$Hydrocarbons \xrightarrow{O_2} CO_2 + H_2O$$

$$(unburnt petrol)$$

$$2NO \xrightarrow{Catalyst} N_2 + O_2$$

5.3.3 THEORIES OF CATALYSIS

There is no universal principle behind the action of catalysts as catalytic reactions are of varied nature. However, two broad theories of catalytic action have been proposed. These are as follows:

a. Intermediate compound formation theory: It was proposed by Clement and Desormes in 1806. It successfully explains the homogeneous catalysis.

According to this theory, the catalyst first forms an intermediate compound with one of the reactants, which then decomposes or combines with another reactants to produce the product and the catalyst is regenerated. The catalyst in this reaction lowers the free energy of activation and hence accelerates the rate of reaction.

For example, the oxidation of SO₂ to SO₃ in the presence of NO takes place as follows:

This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction is effective in small quantities.

However, this theory is limited to homogeneous catalysis as the formation of intermediate compound is possible in the case of homogeneous catalysis only. It also fails to explain the action of catalytic promoters, catalytic poisons, and action of finely divided catalyst.

b. Adsorption theory: This theory explains the mechanism of heterogeneous catalysis. According to the earlier adsorption theory of heterogeneous catalysis, it was believed that the reactants in gaseous state or in solutions, are adsorbed on the surface of the solid catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is utilized in enhancing the rate of the reaction. This earlier theory does not explain the specificity of a catalyst.

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localized on the surface of the catalyst. The mechanism involves five steps:

- Diffusion of reactants to the surface of the catalyst
- Adsorption of reactant molecules on the surface of the ii. catalyst
- iii. Occurrence of chemical reaction on the catalyst's surface through the formation of an intermediate (Fig. 5.12)
- iv. Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur
- Diffusion of reaction products away from the catalyst's surface

The surface of the catalyst unlike the inner part of the bulk has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for fresh reactant molecules.

In case free valencies are responsible for the catalytic activity, it follows that with the increase of these valencies on the surface of a catalyst, the catalytic activity will be greatly enhanced. The free valencies can be increased in the following two ways:

- 1. By fine division of the catalyst
- 2. By rough surface of the catalyst

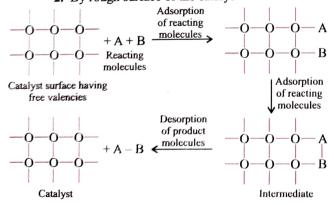


Fig. 5.12 Adsorption of reacting molecules, formation of intermediate, and desorption of products

This theory does not explain the action of catalytic promoters and catalytic poisons.

5.3.4 IMPORTANT FEATURES OF SOLID CATALYSTS (HETEROGENEOUS CATALYST)

The effectiveness of a catalyst depends upon two important aspects: activity and selectivity.

a. Activity of a catalyst: Activity is the ability of a catalyst to accelerate the rate of a chemical reaction.

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactant must adsorb reasonably strongly for the catalyst to be active but must not adsorb so strongly that they become immobilize and the other reactants do not get space on the catalyst surface for adsorption. It has been observed that for hydrogenation, the catalytic activity increases as we go from Group 5 metals to Group 11 metals with maximum activity shown by elements of Group 7-9 in the periodic table.

A catalyst may accelerate a reaction to as high as 10^{10} times. For example, the mixture of H_2 and O_2 can be stored for any period but in the presence of platinum, the reaction occurs with explosive violence.

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(g)$$

b. Selectivity of a catalyst: The selectivity of a catalyst is its ability to direct a reaction to yield a particular product For examples, starting with H₂ and CO, and using different catalysts, we get different products.

i.
$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

ii.
$$CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$$

iii.
$$CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$$

Similarly, acetylene on reaction with H₂ in the presence of Pt catalyst gives ethane, while in the presence of Lindlar's catalyst (palladium and BaSO4 poisoned with quinoline or sulphur) gives ethylene.

$$H - C = C - H + H_{2}$$

$$Acetylene$$

$$Lindlar's catalyst CH_{3} - CH_{3}$$

$$Ethane$$

$$CH_{2} = CH_{2}$$

$$Ethylene$$

Thus, it can be inferred that the action of a catalyst in highly selective in nature, i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means that a substance which acts as a catalyst in one reaction may fail to catalyze another reaction.

5.3.5 SHAPE-SELECTIVE CATALYSIS BY ZEOLITES

Zeolites are naturally occurring or synthetic microporous aluminosilicates of general formula:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]_m \cdot H_2O$$

 $M = Na^{\oplus}$, K^{\oplus} , or Ca^{2+} -like metals

n =Valency of metal cation

m = molecules of water of crystallization

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules and shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honeycomb-like structures. Selective are aluminosilicates, i.e., three-dimensional network reolites are aluminosilicates, i.e., three-dimensional network reolites in which some silicon atoms are replaced by aluminium silicates in which some silicon atoms are replaced by aluminium. They are found in nature as well as synthesized for along. They are found in nature as well as synthesized for selectivity. Zeolites, before using as catalyst, are heated catalytic selectivity. Zeolites, before using as catalyst, are heated catalytic selectivity. It was not the water of hydration is lost. As a result, in vacuum so that the water of hydration is lost. As a result, which were occupied by the water molecules become vacant. Which were occupied by the water molecules become vacant. The size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and the size of the pores generally varies between 260 pm and th

The reaction taking place in zeolites depend upon the size and taking place in zeolites depend upon the size and taking place in zeolites as well as upon the pores and cavities of the zeolites. That is why these types of reactions are called *shape-selective catalysis* reactions.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and somerization. An important zelolite catalyst in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them so that a mixture of hydrocarbons is formed.

5.4 ENZYME CATALYSIS

Living organisms carry out thousands of chemical reactions which take place in dilute solution at ordinary temperature and pressure. For example, they can use small molecules to assemble complex biopolymers such as proteins and DNA. Organisms can produce molecules that combat bacterial invaders. They can break down large, energy-rich molecules in many steps to extract chemical energy in small portions to drive most of their activities.

Most of these reactions are catalyzed by biochemical catalysts called enzymes. Enzymes are proteins with high molar mass ranging from 15000 to 1000000 g mol⁻¹. Enzymes are incredibly efficient catalysts. They increase rates by 10⁸ to 10²⁰ times. Enzymes are also extremely specific: each reaction is senerally catalyzed by a particular enzyme. Urease, for example, catalyzes only the hydrolysis of urea and none of the several thousand other enzymes present in the cell catalyzes that reaction.

$$NH_2CONH_2 + H_2O \xrightarrow{Urease} 2NH_3 + 2CO_2$$

Most enzymes have been obtained in pure crystalline state from living cell. However, the first enzyme was synthesized in the laboratory in 1969.

Following are some of the examples of enzyme-catalyzed feactions:

^{a.} Inversion of cane sugar: The invertase enzyme converts cane sugar into glucose and fructose.

$$\begin{array}{c} \text{C_{12}H$}_{22}\text{$O_{11}$}(\text{aq}) + \text{$H_2$}\text{$O(1)$} \xrightarrow{\text{Invertase}} \\ \text{$C_{ane sugar}$} & C_6\text{H_{12}}\text{O_6}(\text{aq}) + C_6\text{H_{12}}\text{O_6}(\text{aq}) \\ & \text{Glucose} & \text{Fructose} \end{array}$$

b. Conversion of glucose into ethyl alcohol: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$C_6H_{12}O_6(aq) \xrightarrow{Zymasc} 2C_2H_5OH(aq) + 2CO_2(g)$$
Glucose Ethyl alcohol

c. Conversion of starch into maltose: The diastase enzyme converts starch into maltose.

$$2(C_6H_{10}O_5)_n(aq) + nH_2O(1) \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}(aq)$$
Starch
Maltose

d. Conversion of maltose into glucose: The maltase enzyme converts maltose into glucose.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6(aq)$$
Maltose Glucose

e. Decompostion of urea into ammonia and carbon dioxide:
The enzyme urease catalyzes this decomposition.

$$NH_2CONH_2(aq) + H_2O(l) \xrightarrow{Urease} 2NH_3(g) + CO_2(g)$$

- f. Catalysis by pepsin and trypsin: In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.
- **g.** Conversion of milk into curd: It is an enzymatic reaction brought about by lactobacilli enzyme present in curd.

Table 5.4 gives the summary of some important enzymatic reactions.

Enzymatic reaction Source Enzyme Sucrose → Glucose and fructose Yeast Invertase Glucose → Ethyl alcohol and Yeast **Zymase** carbon dioxide → Maltose Diastase Malt Starch Yeast Maltose → Glucose Maltase Soyabean Urea → Ammonia and carbon Urease dioxide Pepsin Stomach Proteins → Amino acids

Table 5.4 Some enzymatic reactions

5.4.1 CHARACTERISTICS OF ENZYME CATALYSIS

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

- a. High efficiency: Enzymes are efficient catalyst. Even one molecule of an enzyme may transform one million molecules of the reactant per minute.
- b. High specificity: The enzyme catalysts are highly specific in nature. Almost every biochemical reaction is controlled by its own specific enzyme, i.e., one enzyme cannot catalyze more than one reaction. For example, the enzyme urease catalyzes the hydrolysis of urea only. It does not catalyze hydrolysis of any other amide.
- c. Temperature dependence: The rate of an enzyme reaction becomes maximum at a definite temperature, called the

optimum temperature. On either side of the optimum, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298–310 K. Human body temperature being 310 K is suited for enzyme-catalyzed reactions.

- **d. pH dependence:** The rate of an enzyme-catalyzed reaction is maximum at a particular pH called optimum pH, which is lies between 5 and 7.
- e. Presence of activators and co-enzymes: The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, catalytic activity is enhanced considerably.

Activators are generally metal ions such as Na^{\oplus} , $Mn^{2^{+}}$, $Co^{2^{+}}$, $Cu^{2^{+}}$, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride, i.e., Na^{\oplus} ions, is catalytically very active.

f. Influence of inhibitors and poisons: Like ordinary catalysis, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduced or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

5.4.2 MECHANISM OF ENZYME CATALYSIS

The remarkable specificity of enzymes results from the fact that each enzyme has a specific, active site on its surface such as—NH₂,—COOH,—SH,—OH, etc. These are actually the active centres on the surface of enzyme particles; when the reactant molecules, called the substance of the reaction, bind at the active site, a chemical change is initiated and an activated complex is formed which then decomposes to yield the products. In most cases, the substrate binds to the active site through intermoleuclar forces: H-bonds, dipole forces, and other weak attractions.

Two models of enzyme action have been proposed (Fig. 5.13):

a. Lock and key modelb. Induced fit model

According to the *lock and key model*, every lock (active site) has a particular shape and when a particular key (substrate), which has complementary shape, fits into a lock, the chemical change begins, which finally results into a product (Fig. 5.13).

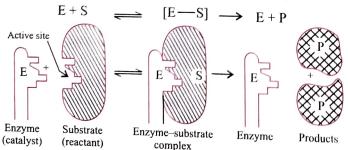


Fig. 5.13 Mechanism of enzyme-catalyzed reaction

Modern X-ray crystallographic and spectroscopic methods have shown that in many cases, unlike an ordinary lock, the protein

molecules (enzyme) slightly change the shape when a substrate lands at the active site. The ability of an enzyme to undergo the correct distortion also determines whether the "key" will fit or not. This refinement of the original lock-and-key model is known as induced fit model. According to this model, a substrate induces the active site to adopt a perfect fit rather than a rigidly shaped lock and key. Therefore, we can picture this model as hand in a glove, in which the glove (active site) does not attain its functional shape until the hand (substrate) moves into place.

The kinetics of enzyme catalysis has many features in common with ordinary catalysis. In the enzyme-catalyzed reaction, substrate (S) and enzyme (E) form an intermediate enzyme-substrate complex (ES) whose concentration determines the rate of product (P) formation. The steps common to virtually all enzyme-catalyzed reactions are:

Step 1: Binding of enzyme to substrate to form an activated complex.

$$E + S \longrightarrow ES^{\neq}$$
 (Fast, reversible)

Step 2: Decomposition of the activated complex to form product, $ES^{\neq} \longrightarrow E + P$ (Slow, rate determining)

The rate of enzyme-catalyzed reaction changes from first order to zero-order as the concentration of substrate is increased

5.4.3 CATALYSTS IN INDUSTRY

The enzymes are widely used in industrial processes. Some of the important catalytic processes are listed in Table 5.5 to give an idea about the utility of catalysts in industries.

Table 5.5 Some industrial catalytic processes

Table 5.5 Some industr	rial catalytic processes
Process	Catalyst
1. Haber's process for the	Finely divided iron, molybdenum
manufacture of ammonia	as promoter; condition: 200 bar
$N_2(g) + 3H_2(g) \rightarrow$	pressure and 723-773 K
2NH ₃ (g)	temperature. Now-a-days, a
	mixture of iron oxide, potassium
	oxide, and alumina is used.
2. Ostwald's process for the	Platinized asbestos:
manufacture of nitric acid.	temperature 573 K
$4NH_3(g) + 5O_2(g)$	
\rightarrow 4NO(g) + 6H ₂ O(g)	
$2NO(g) + O_2(g)$	
$\rightarrow 2NO_2(g)$	
$4NO_2(g) + 2H_2O(1) + O_2(g)$	
\rightarrow 4HNO ₃ (aq)	
3. Contact process for the	Platinized asbestos or vanadium
manufacture of sulphuric	pentoxide (V ₂ O ₅): temperature
acid.	673–723 K.
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	
$SO_3(g) + H_2SO_4(aq)$	
$\rightarrow H_2S_2O_7(aq)$	
Oleum	
$H_2S_2O_7(1) + H_2O(1)$	2

 $\rightarrow 2H_2SO_4(aq)$

LLUSTRATION 5.22 Why is it necessary to remove CO when ammonia is obtained hy Haber's process?

CO acts as a poison for the catalyst used in the manufacture CUaciona by Haber's process. Hence, it is necessary to remove it.

ILUSTRATION 5.23 Why is ester hydrolysis slow in the beginning and becomes faster after some time?

The ester hydrolysis takes place as follows:

The ester hydrolysis takes place as follows:

$$RCOOR' + H_2O \Longrightarrow RCOOH + R'OH$$

Water Acid Alcohol

The acid produced in the reaction acts as catalyst (autocatalyst) for the reaction. Hence, the reaction becomes faster after some time.

ILLUSTRATION 5.24

What do you mean by activity of catalysts?

Activity is the ability of catalysts to accelerate chemical reactions.

LUSTRATION 5.25

How does BF₃ act as a catalyst in industrial process?

BF₃ is a strong Lewis acid. Hence, it is used as a catalyst in industrial processes.

LUSTRATION 5.26

Give an example of a shape-selective catalyst.

Zeolites are shape-selective catalysts. A zeolite called ZSM-5 converts alcohol to gasoline.

LLUSTRATION 5.27

Explain the shape-selective catalysis.

The catalystic reaction which depends upon the pore size of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective catalysts because of their honey comb like structures. ZSM-5 is used in petroleum industry to convert alcohols directly into gasoline by dehydrating them to give a mixture of hydrocarbons.

$$xCH_3$$
—OH $\xrightarrow{ZSM-5}$ $(CH_2)_x + xH_2O$
Gasoline

LLUSTRATION 5.28

What is the role of desorption in the process of catalysis?

Sol. Desorption makes the surface of a solid catalyst free for fresh adsorption of reactants on the surface.

ILLUSTRATION 5.29

- i. The ability of a catalyst to direct the reaction to yield particular products is called d. Fugacity
 - a. Reactivity b. Selectivity c. Activity
- ii. Which of the following is an example of zeolite? d. Co(OH)₂
 - c. $Mg(OH)_2$ b. AgNO3 a. ZSM-5
- iii. Reactions in zeolite catalyst depend on
 - a. Pores
- b. Apertures

iii. d.

- c. Size of cavities
- d. All of these
- Sol. i. b.

ILLUSTRATION 5.30

Taking two examples of heterogeneously catalyzed reactions, explain how a heterogeneous catalyst helps in the reaction.

- Sol. Solid catalysts are used in a number of gaseous reactions. Such catalytic reactions are called heterogeneous reactions. Examples of heterogeneous catalysis are as follows:
 - a. Manufacture of ammonia from N₂ and H₂ by Haber's process in the presence of catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

b. V_2O_5 catalyst is used in the manufacture of H_2SO_4 by contact process.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$$

Solid catalyst helps in the following ways:

- Simultaneous adsorption of reactants increases with concentration at the surface of the catalyst which increases the reaction rate.
- ii. Adsorption of reactant molecules makes the attack of other molecules on it easier.
- iii. Some adsorbed molecules dissociate into atoms which are very reactive.
- iv. The heat of adsorption released provides activation energy for the reaction.

ILLUSTRATION 5.31

Give four examples of heterogeneous catalytic reactions.

Sol.

- a. Contact process reactions
- **b.** Haber's process reactions
- c. Hydrogenation of vegetable oils

Vegetable oil +
$$H_2 \xrightarrow{Ni}$$
 Vegetable ghee

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$$

d. Synthesis of methanol

Synthesis of Hermanov

$$CO(g) + 2H_2(g) \xrightarrow{Cu, ZnO - Cr_2O_3} CH_3OH(l)$$

ILLUSTRATION 5.32

How does the rate of an enzyme-catalyzed reactions vary with (a) temperature and (b) pH? Represent diagrammatically.

Sol. As the temperature or pH is increased, the rate rises till it is maximum at 37°C (physiological temperature) or pH = 7.4 and then falls off (as shown in the figure).

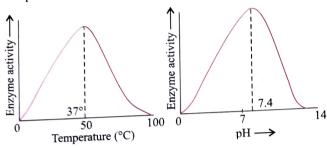


ILLUSTRATION 5.33

Indicate a chemical reaction involving a homogeneous catalyst.

Sol.
$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

ILLUSTRATION 5.34

How does a catalyst work?

Sol. It provides an alternate path involving lower activation energy for the reactants.

ILLUSTRATION 5.35

What do you mean by activity and selectivity of catalyst?

Sol. Activity is the ability of a catalyst to accelerate chemical reactions, for example, Pt catalyzes the combination of H2 and O2 to form water. It has been found that for hydrogenation reactions, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by Group 7-9 elements of the periodic table.

Selectivity is the ability of a catalyst to direct a reaction to yield a particular product. A combination of CO and H2 yields different products with different catalysts as given below:

$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

$$CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$$

$$CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$$

ILLUSTRATION 5.36

- i. Which of the following small-sized elements can replace silicon and aluminium in the framework at zeolites
 - a. Boron
- b. Magnesium
- c. Phosphorus
- d. All

- ii. Zeolites are microporous aluminosilicates with general formula
 - a. $M[(AlO_2)_x] \cdot mH_2O$
 - **b.** $M_{\nu}[(AlO_2)_{\nu}(SiO_2)_{\nu}]$
 - c. $M_x[(SiO_2)_v] \cdot mH_2O$
- **d.** $M_{x/n}[(AIO_2)_x(SiO_2)_y] \cdot mH_2O$ iii. The zeolites have shape selectivity depending on
 - b. Atomic structure
 - a. Pore structure
 - d. None c. Molecular structure

Sol.

- i. d
- ii. d
- iii. a

ILLUSTRATION 5.37

A catalyst lowered the activation energy by 25 kJ mol-1 at 25°C. By how many times will the rate grow?

Sol. The rate of reaction is related to the activation energy by the following relation:

the following relativistic following
$$\frac{K_2}{K_1}$$
 = Antilog $\left[\frac{\Delta E}{2.303RT}\right]$...(i)

Given,
$$\Delta E = 25 \times 10^3 \text{ J}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 25^{\circ}\text{C} = 298 \text{ K}$$

Substituting all the values in Eq. (i), we get

$$\frac{K_2}{K_1} = \text{Antilog} \left[\frac{25 \times 10^3}{2.303 \times 8.314 \times 298} \right] = 24069$$

$$K_2 = K_1 \times 24069$$

Therefore, the rate increases by 24069 times.

ILLUSTRATION 5.38

At 400 K, the energy of activation of a reaction is decreased by 0.8 kcal in the presence of catalyst. Hence, the rate will be

- a. Increased by 2.73 times
- b. Increased by 1.18 times
- c. Decreased by 2.72 times
- d. Increased by 6.26 times

Sol.

a. We know

$$\frac{K_2}{K_1} = \text{Antilog}\left[\frac{\Delta E}{2.303RT}\right] \qquad ...(i)$$

Given
$$\Delta E = 0.8 \text{ kcal} = 3.344 \times 10^3 \text{ J}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 400 \text{ K}$$

Substituting all the values in Eq. (i), we get

$$\frac{K_2}{K_1}$$
 = Antilog $\left[\frac{3.344 \times 10^3}{8.314 \times 2.303 \times 400} \right] = 2.73$

$$K_2 = 2.73 K_1$$

Therefore, the rate will increase by 2.73 times.

55 COLLOIDS

he foundation of colloidal chemistry was laid down by an English Thomas Graham, in 1861. 1860 following fraham, in 1861.

Thomas Graham classified the soluble substances into two Thomas Oriminates are of their diffusion through animal animal membranes or parchment paper. He also animal membranes or parchment paper. and regerates depending or parchment paper. He observed that and regerates diffuse freely through the membranes paper. He observed that represent the paper of substances diffuse freely through the membrane, whereas a substance at all. The former type of substances in the membrane, whereas at all. The former type of substances on account where a such as common salt and a such as common salt as common salt as common salt as common salt a and crystalloids while the latter type were town. their crystalloids while the latter type were termed as colloids while the latter type were termed as colloids. more were termed as colloids word, kola, meaning glue-like). All inorganic acids, bases, and organic compounds such as such word and organic compounds such as sugar, urea, etc., were and salls and crystalloids while substances such as starch, gelatine, while substances to the collected silicic acid, etc., belonged to the colloidal group.

lt was soon realized that the above classification was not since many crystalline substances can be converted into alloidal form by suitable means. The colloidal form of sodium a crystalloid, can be obtained in benzene. Thus, the above issification was discarded, i.e., the term colloid does not apply particular class of substances but is a state of matter such as glid liquid, and gas. Any substance can be brought into colloidal by suitable means. Therefore, there is no separate class of substances called colloidal substance. It is just a state of matter into which every substance can be obtained by a suitable method. Further studies of the behaviour of these solutes have shown that the nature of a substance whether crystalloid or colloid depends upon the size of the solute particles. When the size of the solute particles lies between 1 nm and 100 nm it behaves like a colloid. If the size of solute particles is greater than 100 nm, it exists as suspension, and if the particle size is less than 1 nm, it exists as a true solution.

Thus, a colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium. In a colloid, the dispersed phase may consist of particles of a single macromolecule (such as synthetic polymer or protein) or an aggregate of many atoms, molecules, or ions.

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm². If it were divided equally into 1012 cubes, the cubes would be the size of large colloidal particles and have a total surface area of 60000 cm² or 6 m². This enormous surface area leads to some special properties of colloids to be discussed later in this chapter.

The distinction between characteristics of suspension, colloidal solution, and true solution is tabulated in Table 5.6.

Table 5.6 Difference between suspension	colloidal solution, and true solution

. 11-	Property	True solution	Colloidal solutions	Suspension
S.No. 1.	Particle size	Less than 10 ⁻⁹ m or 1 nm (i.e., <10 Å)	Between 10 ⁻⁹ and 10 ⁻⁷ m or 1 nm and 100 nm	More than 10 ⁻⁷ m or 100 nm (i.e., >1000 Å)
2.	Filterability	Pass through ordinary filter paper as well as animal membrane	Pass through ordinary filter paper but not through animal membrane	Do not pass through filter paper as well as animal membrane
3.	Settling	Do not settle	Do not settle	Settle on standing
4.	Visibility	Particles are invisible	Scattering of light by the particles is observed under ultra-microscope.	Particles are visible to naked eye or under a microscope.
5.	Diffusion	Diffuse quickly	Diffuse slowly	Do not diffuse
6.	Appearance	Clear and transparent	Transluscent	Opaque

5.5.1 CLASSIFICATION OF COLLOIDS

Colloids are classified on the basis of following criteria:

- a. Physical state of dispersed phase and dispersion medium
- b. Nature of interaction between dispersed phase and dispersion medium
- c. Type of particles of the dispersed phase

Colloidal solution is heterogeneous in nature and always consists of at least two phases, namely, disperse phase and dispersion medium. The component present in small proportion and consisting of particles of colloidal dimensions is called disperse phase. The medium in which colloidal particles are dispersed is called dispersion medium.

Classification Based on the Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids, or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 5.7.

It is clear from Table 5.7 that many common commercial products and natural objects are colloids. For example, whipped cream is a colloidal system (foam), a gas dispersed in a liquid. Out of the different types of colloids, the most common are sols (solids in liquids), gels (liquids in solids), and emulsions (liquids in liquids).

Table 5.7 Types of colloidal system

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid Solid Liquid Liquid Liquid	Liquid Gas Solid Liquid Gas	Sol Aerosol Gel Emulsion Aerosol	Paints, cell fluids Smoke, dust Cheese, butter, jellies Milk, hair cream Fog, mist, cloud, insecticide
Gas Gas	Solid Liquid	Solid sol Foam	sprays Pumice stone, foam rubber Froth, whipped cream, soap lather

Depending upon the nature of the dispersion medium, colloidal solutions are sometimes given specific names. For example:

Dispersion medium	Name of colloidal solution	
Water	Hydrosols	
Alcohol	Alcosols	
Benzene	Benzosols	
Air	Aerosols	

Classification Based on the Nature of Interaction between Dispersed Phase and Dispersion Medium

Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, *lyophilic* (solvent attracting) and *lyophobic* (solvent repelling). If water is a dispersion medium, the terms used are hydrophilic and hydrophobic.

- a. Lyophilic colloids: The word lyophilic means liquid-loving. Colloidal sols directly formed by mixing substances such as gum, gelatine, starch, rubber, etc., with a suitable liquid (the dispersion medium) are called lyophilic sols. As they form the colloidal sol directly they are also called intrinsic colloids. An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called reversible sols. Furthermore, these sols are quite stable and cannot be easily coagulated as discussed later.
- b. Lyophobic colloids: The word *lyophobic* means liquid-hating. Substances such as metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods (as discussed later). Such sols are called lyophobic sols. As their colloidal sols have to be prepared by indirect methods, they are also called extrinsic colloids. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and, hence, are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, these sols are also called *irreversible sols*. Lyophobic sols need stabilizing agents for their preservation.

The essential difference between lyophilic sols and lyophobic sols are given in Table 5.8.

Table 5.8 Difference between lyophilic sols and lyophobic sols

	Table 5.8 Difference between tyophine 3013 and tyophiode 3013				
S. No.	Property	Lyophilic sol	Lyophobic sols		
1.	Ease of preparation	Prepared easily by directly mixing with the liquid dispersion medium.	Cannot be prepared directly. Prepared by special methods only.		
2.	Stability	They are quite stable and are not easily precipitated or coagulated.	They are easily precipitated by addition of a small amount of a suitable electrolyte.		
3.	Reversible and irreversible nature	They are reversible in nature, i.e., once precipitated can reform the colloidal solution by simply remixing with the dispersion medium.	They are irreversible in nature, i.e., once precipitated cannot form the colloidal solution by simple addition of the dispersion medium.		
4.	Nature of substances	These sols are usually formed by organic substances such as starch, gum, proteins, etc.	These sols are usually formed by inorganic materials such as metals, their sulphides, etc.		

5.	Viscosity	Their viscosity is much higher than that of the medium.	Their viscosity is almost the same as that of the medium.
6.	Surface tension	Their surface tension is usually lower than that of the dispersion medium.	Their surface tension is nearly same as that of the dispersion medium.
1.	Visibility	Their particles are neither visible nor detected easily by an ultra-microscope (by the scattering of light).	Their particles, though not visible, can be easily detected by an ultra-microscope.
	Migration in an electric field	Their particles may migrate in either direction or may not migrate at all.	Their particles migrate in only one particular direction in the electric field.

$_{\text{Dispersed}}$ Phase

Depending upon the type of particles of the dispersed phase, the colloids are classified as:

- a. Multimolecular colloids
- b. Macromolecular colloids
- c. Associated colloids
- a. Multimolecular colloids: When on dissolution a large number of atoms or smaller molecules of a substance (with diameter less than 1 nm) aggregate together to form species having size falling in the colloidal range, the species thus formed are called multimolecular colloids. The dispersed phase in this type of colloidal system may contain large aggregates of atoms of molecules formed as a result of aggregating properties of the dispersing particles. For example, a gold sol may contain particles of various sizes having several atoms. Sulphur sol consists of particles containing a thousand or so of S₈ sulphur molecules. These are held together by van der Waals forces.
- big size molecular colloids: When certain substances having big size molecules, called macromolecules having large molecular masses, are dissolved in a suitable liquid, they form a solution in which the molecules of the substance, i.e., the dispersed particles, have size falling in the colloidal range. Such substances are called macromolecular colloids. The macromolecular substances are usually polymers with very high molecular masses. Examples of naturally occurring macromolecules are starch, cellulose, proteins, enzymes, and gelatin.

Examples of man-made macromolecules are polyethylene, nylon, polystyrene, synthetic, rubber, etc. As these

- molecules have large sizes and have dimensions comparable to those colloidal particles, their dispersions are called macromolecular colloids. Their colloidal solutions are quite stable and resemble true solutions in many respects.
- c. Associated colloids (micelles): There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids. The formation of micelles takes place only above a particular temperature called Kraft temperature (T_K) and above a particular concentration called critical micelle concentration (CMC). On dilution, these colloids revert back to ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is 10^{-4} to 10^{-3} mol L⁻¹. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

Mechanism of micelle formation

Micelles are generally formed by the aggregation of several ions or molecules with lyophilic as well as lyophobic parts. Let us take the example of soap solutions. Soap is a sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^{\circ}N^{\oplus}$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^{\circ}Na^{\oplus}$, which is a major component of many bar soaps). When dissolved in water, it dissociates into $RCOO^{\circ}$ and Na^{\oplus} ions. The $RCOO^{\circ}$ ions, however, consist of two parts—a long hydrocarbon chain R (also called non-polar "tail") which is hydrophobic (water repelling), and a polar group COO° (also called polar-ionic "head"), which is hydrophilic (water loving).



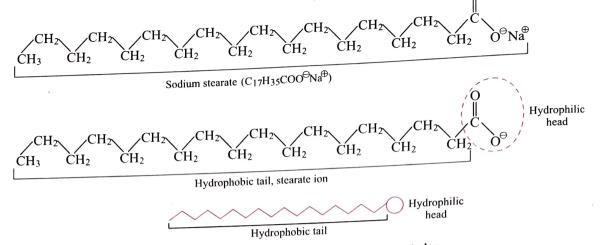


Fig. 5.14 Hydrophobic and hydrophilic parts of stearate ion

The RCOO[□] ions are, therefore, present on the surface with their COO[□] groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with COO[□] part remaining outward on the surface of the sphere. An aggregate thus formed is known as *ionic micelle*. These micelles may contain as many as 100 such ions.

Similarly, in case of detergents. e.g., sodium laurylsulphate, $\mathrm{CH_3(CH_2)_{11}SO_4}^{\odot}\mathrm{Na^{\oplus}}$, the polar group is $-\mathrm{SO_4}^{\odot}$, along with the long hydrocarbon chain. Hence, the mechanism of micelle formation here also is same as that of soaps.

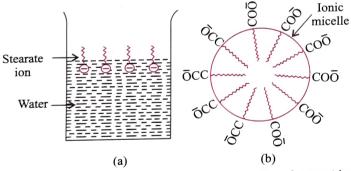


Fig. 5.15 (a) Arrangement of stearate ions on the surface of water at low concentrations of soap

(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

Some other examples of micelle systems are as follows:

- i. Sodium lauryl sulphonate CH₃[CH₂]₁₁ SO₃[⊙]Na[⊕]
- ii. Sodium oleate $C_{17}H_{33}COO^{\odot}Na^{\oplus}$
- iii. Cetyl trimethyl ammonium bromide $CH_3(CH_2)_{15}N^\oplus(CH_3)_3Br^\circleddash$
- iv. p-Dodecyl benzene sulphonate

$$C_{12}H_{25} \hspace{-2pt} -\hspace{-2pt} \hspace{-2pt} \hspace{-2pt$$

Cleansing action of soaps

The cleansing action of soap is due to the fact that soap molecules form micelles around the oil droplet in such a way that the hydrophobic part of stearate ions is in the oil droplet and the hydrophilic part projects out of the grease droplet like the bristles (Fig. 5.16).

When a piece of cloth is dipped in aqueous soap solution, the soap and the dirt come in contact with each other. The non-polar end (tail) dissolves in the grease deposit while the polar end (—COO® or head) is directed towards water. In this manner, each oil droplet is surrounded by a number of negatively charged carboxylate ions. Since similar charges repel each other, the oil droplets break up and form small droplets. These small droplets get dispersed in water forming an emulsion. The hand rubbing or the agitation due to washing machine causes dispersion of the oil or grease throughout the soapy water. These are washed away with water along with dust particles. In this way grease or din are removed from the surface of the cloth.

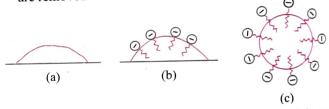


Fig. 5.16 (a) Grease on cloth, (b) stearate ions arranging around the grease droplet, and (c) grease droplet surrounded by stearate ions (micelle formed)

The important differences between multimolecular, macromolecular, and associated colloids are listed in Table 5.9.

Table 5.9 Differences between multimolecular, macromolecular and associated colloids

Mı	ultimolecular colloids	Macromolecular colloids	Associated colloids
ag or ge di	hey consist of agregates of atoms molecules which enerally have ameter less an 1 nm.	They consist of large molecules (generally polymers)	They behave as colloidal size particles at higher concentrations.
m he va	he atoms or olecules are eld by weak an der Waals orces.	The molecules are flexible and can take any shape.	They behave as normal electrolytes at low concentrations.
	hey have usually ophilic character.	They have usually lyophobic character.	Their molecules contain both lyophilic and lyophobic groups

preparation of Colloidal Solutions 5.2 r ... (or sols) are generally ophilic and lyophobic colloidal solutions (or sols) are generally different types of methods. Some of the ophilic and types of methods. Some of the common by different types of methods. Some of the common to are as follows:

ulhods are as follows: preparation of lyophilic sols: The lyophilic sols can be prepared directly by mixing a substance with a market directly by mixing a market directly by mixing a substance with a market directly prepared directly by mixing a substance with a dispersion For example, colloidal solo prepared. For example, colloidal sols of starch, gelatin, medium. For example, are prepared by medium. arabic, soaps, etc., are prepared by simply dissolving gum and substances in warm water. Similarly, a colloidal sol. these successful alcohol. The product is an organic of centrols of all all of solvent such as ethyl alcohol. The product obtained is called

preparation of lyophobic sols: To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension (1 Å to 10³ Å) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called stabilizers. Thus, there are two ways by which lyophobic sols can be prepared.

i. Dispersion methods: By splitting coarse aggregates of a substance into colloidal size.

ii. Condensation methods: By aggregating very small particles (atoms, ions, or molecules) into colloidal size.

i. Dispersion or disintegration methods: The methods involves the breaking of bigger particles into colloidal size. The methods generally employed for this purpose are briefly described below.

1. Mechanical disintegration: The mechanical disintegration is carried out in a machine called colloid mill. It consists of two steel discs with a little gap in-between and capable of rotating in the opposite direction at a very high speed (about 7000 revolutions per minute). Solid material is first finely ground by usual method.

It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (lubricant) and printing ink are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink).

Note: • This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.

This method comprises both dispersion and condensation.

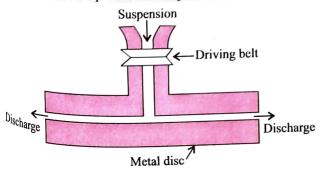


Fig. 5.17 Colloidal mill

2. Electrical disintegration or Bredig's Arc method: This method is employed for obtaining colloidal solutions of metal such as gold, silver, platinum, etc. In this method, an electric arc is struck between two metallic electrodes, immersed in the dispersion medium (Fig. 5.18). The intense heat produced vapourizes some of the metal, which then condenses to form particles of colloidal size. The colloidal solution prepared is stabilized by adding a small amount of KOH to it. This process involves dispersion as well as condensation.

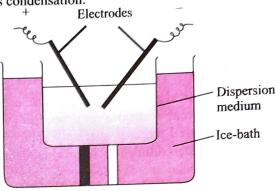


Fig. 5.18 Bredig's arc method

3. Peptization: Peptization may be defined as the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

A few examples of sols obtained by peptization are given below:

- A reddish brown coloured colloidal solution is obtained by adding small quantity of ferric chloride solution to the freshly precipitated ferric hydroxide.
- A precipitate of silver iodide can be peptized by shaking with a dilute solution of silver nitrate or
- On adding insufficient quantity of very dilute HCl solution to the freshly precipitated aluminium hydroxide, a sol of aluminium hydroxide is obtained.

Causes of peptization: During peptization, the precipitate adsorbs one of the ion of the electrolyte on its surface. The adsorbed ion is generally common with those of precipitate. This causes the development of positive or negative charge on the precipitates, which ultimately breaks into particles of colloidal dimensions. For example, when freshly precipitated ferric hydroxide is shaken with aqueous solution of ferric chloride (peptizing agent), it adsorbs Fe³⁺. Similarly, a precipitate of AgCl on shaking with dilute solution of AgNO3 adsorbs Ag[®] ion and get peptized to colloidal particles of the type [AgCl]Ag[®]. In some cases, peptization can also be achieved by organic solvents. For example, cellulose nitrate is peptized by ethanol. The colloidal solution of cellulose nitrate in ethanol is called colloidion.

- ii. Condensation method: In these methods, smaller particles of dispersed phase are condensed suitably to be colloidal size. This is done by the following methods:
 - 1. By exchange of solvent: If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.
 - 2. By change of physical state: Colloidal solutions of certain elements such as mercury and sulphur are obtained, passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate).
 - 3. Chemical methods: The chemical method involves chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super-saturation is produced but the actual precipitation is avoided.
 - Double decomposition: A colloidal solution of arsenic sulphide is obtained by passing hydrogen sulphide into a solution of arsenic oxide in distilled water.

 $As_2O_3 + 3H_2O \longrightarrow As_2S_3$ (yellow sol) + $3H_2O$ Sols of silver halide are obtained by mixing dilute solutions of silver salts and alkali metal halides in equivalent amounts.

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

Oxidation: A colloidal solution of sulphur can be prepared by passing hydrogen sulphide into a solution of sulphur dioxide in water or through a solution of an oxidizing agent such as bromine water or nitric acid.

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S \text{ (sol)}$$

Sulphur sol can also be obtained when H₂S is bubbled through an oxidizing agent (bromine water or nitric acid).

Reduction: A colloidal solution of a metal such as silver, gold, or platinum can be prepared by the reduction of its salt solution with a suitable reducing agent such as stannous chloride, formaldehyde, hydrazine, etc.

$$\begin{aligned} &2\text{AuCl}_3 + 3\text{SnCl}_2 \longrightarrow 2\text{Au (Gold sol)} + 3\text{SnCl}_4 \\ &4\text{AgCl} + \text{N}_2\text{H}_4 \longrightarrow 4\text{Ag (Silver sol)} + \text{N}_2 + 4\text{HCl} \\ &2\text{PtCl}_4 + 4\text{SnCl}_2 \longrightarrow 4\text{SnCl}_4 + 2\text{Pt(sol)} \end{aligned}$$

Hydrolysis: By this method hydroxide sols of less electropositive metals such as Fe, Al, or Sn are prepared. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water. $FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 (Red sol) + 3HCl$

5.5.3 Purification of Colloidal Solutions

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities.

The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, of the conformal solution of these soluble therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing impurities to a requisite minimum is known as purification of these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods:

a. Dialysis: The process of separating the particles of colloid from those of crystalloids by means of diffusion through a suitable membrane is called dialysis. Its principle is based upon the fact that colloidal particles cannot pass through a apon the fact that contains a superior while the ions of the parchment or cellophane membrane while the ions of the electrolyte can pass through it. The colloidal solution is taken in a bag made of cellophane or parchment. The bag is suspended in fresh water. The impurities slowly diffuse out of the bag leaving behind pure colloidal solution. The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag. Dialysis can be used for removing HCl from the ferric hydroxide sol. The method is shown in Fig. 5.19.

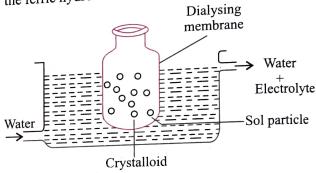


Fig. 5.19 Dialysis

In humans, kidneys perform dialysis in order to purify blood which is of colloidal nature. The most important application of dialysis process is the artificial kidney machine used for the purification of blood of the patients whose kidneys have failed to work.

b. Electro-dialysis: Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. The process is then named electrodialysis. The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in Fig. 5.20. the ions present in the colloidal solution migrate out to the oppositely charged electrodes.

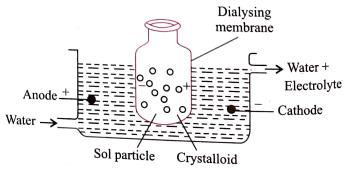


Fig. 5.20 Electrodialysis

c. Ultrafiltration: Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters present in the permeable to all substances except the colloidal which are permeable to all substances except the colloidal which are possible. Colloidal particles can pass through ordinary filter particles. Descause the pores are too large. However, the pores paper can be reduced in size by impart paper pecual paper can be reduced in size by impregnating with of filter particles. of filter particles of colloidion is a 4% solution of colloidal particles. colloidion is a 4% solution of nitrocellulose in a The usual residence in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a colloidion solution, prepared solution, hardening formaldehyde and then finally drying it. Thus, by hardening ultra-filter paper, the colloidal particles are separated using the rest of materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

Ultracentrifugation: In this method, the colloidal solution is placed in a high-speed ultracentrifuge. On centrifuging the colloidal particles settle down. The impurities remain in the dispersion medium and are removed by decantation. The settled colloidal particles are shaken with water containing peptizing agent to form the colloidal solution again.

5.5.4 PROPERTIES OF COLLOIDAL SOLUTIONS

The characteristic properties of colloidal solutions are as given below.

Physical Properties

- a. Heterogeneous nature: A colloidal solution is heterogeneous in nature. It consists of two phases namely, the dispersed phase and the dispersion medium.
- b. Visibility: Colloidal particles are too small to be seen with naked eye, but they become visible as bright spots against dark background when viewed through an ultra microscope due to scattering of light caused by them.
- c. Filterability: The size of solute particles is smaller than the pore size of filter paper, and therefore, they can readily pass through a filter paper. Colloidal particles, however, cannot pass through ultra filters, parchment paper, or animal membrane.
- d. Surface tension and viscosity: The surface tension and viscosity of lyophobic sols are not very different from those of the dispersion medium. On the other hand, lyophilic sols show higher viscosity and lower surface tension in comparison to the dispersion medium.
- e. Colligative properties: A colloidal solution has very small value of mole fraction of dispersed phase due to high average molecular mass of the colloidal particles. As a result of all the colligative properties, colloidal solutions have quite low values when compared to true solutions, having same concentration. However, the low osmotic pressure of a colloidal solution is measurable and can be used to determine the molecular weight of colloidal particles.

Mechanical Properties

a. Brownian movement: The colloidal particles of a colloidal solution when viewed through an ultramicroscope show a constant zig-zag motion. This type of motion was first observed by Robert Brown and is known as Brownian movement (Fig. 5.21). This motion is independent of the nature of the colloid but depends on the size of the particles and the viscosity of solution. Smaller the size and lesser the viscosity, faster is the motion. The motion becomes intense at higher temperature.

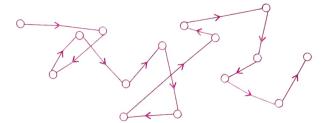


Fig. 5.21 Brownian movement

Cause of Brownian movement

The Brownian movement is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. As the size of the particles increases, the probability of uneven bombardment decreases and the Brownian movement becomes slow. The Brownian movement has a stirring effect which does not permit the particles to settle and, thus, is responsible for the stability of sols.

Importance of Brownian movement

- i. Brownian movement provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.
- ii. It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols by not allowing them to settle down.
- b. Diffusion: colloidal particles such as solute particles of true solution diffuse from a region of higher concentration that of lower concentration. However, colloidal particles diffuse at a slower rate due to their large size and high molecular
- c. Sedimentation: The colloidal particles tend to settle down very slowly under the influence of gravity. The sedimentation or the rate of settling down can be increased by ultracentrifuge.

Optical Properties: Tyndall Effect

The scattering of light by the colloidal particles in a colloidal solution is known as Tyndall effect as it was first observed by Faraday and later studied in detail by Tyndall. Tyndall effect is caused by the scattering of blue part of light by the colloidal particles.

If a strong beam of light is passed through a colloidal solution placed in dark place, the path of the beam gets illuminated. The illuminated path of beam is called Tyndall cone (Fig. 5.22).

The scattering is caused if the size of particles is of the order of wavelength of light. The same effect is not observed when the light is passed through a true solution as the size of solution particles is too small to cause any scattering.

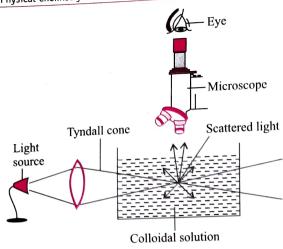


Fig. 5.22 Tyndall effect

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied:

- **a.** The diameter of the dispersed particles is not much smaller than the wavelength of the light used.
- **b.** The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude. This condition is satisfied by lyophobic sols. The lyophilic sols show little or no Tyndall effect as there is very small difference in the refractive indices of the dispersed phase and the dispersion medium.

Zsigmondy, in 1903, used Tyndall effect to set up an apparatus known as ultramicroscope. An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render the actual colloidal particles visible but only observe the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

c. The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of colloidal solution also changes with the manner in which the observer receives the light. For example, a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light. Finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue, and finally golden.

Electric Properties

The colloidal particles always carry an electrical charge. The nature of this charge is same on all the particles in a given colloidal solution and may be either positive or negative. The presence of charge is responsible for the stability of these solutions. It may be noted that only the sol particles carry some charge while the dispersion medium has no charge.

A list of some common sols with the nature of charge on there particles is given below:

Positively charged sols	Negatively charged sols
• Hydrated metallic oxides, e.g., Al ₂ O ₃ ·xH ₂ O, CrO ₃ ·xH ₂ O,	 Metals, e.g., copper, silver gold sols
and Fe ₂ O ₃ ·xH ₂ O • Basic dye stuffs, e.g., methylene blue sol Haemoglobin (blood)	• Metallic sulphides, e.g., As ₂ S ₃ , Sb ₂ S ₃ , CdS sols Acid dye stuffs, e.g., e _{0sin}
• Oxides, e.g., TiO ₂ sol	 congo red sols Sols-of starch, gum, gelating clay, charcoal, etc.

Origin of charges: The charges on the sol particles is due to various reason. Some of these are as follows:

- a. Due to frictional electrification: The mutual rubbing of the dispersed phase particles with that of dispersion medium results in some charge on the colloidal particles.
- b. Due to dissociation of surfactants: For example, dissociation of soap (sodium palmitate) results into ions as: $C_{15}H_{31}COONa \rightleftharpoons C_{15}H_{31}COO^{\odot} + Na^{\oplus}$

The cation (Na^{\oplus}) pass into solution while $a_{\Pi i0\Pi}$ $(C_{15}H_{31}COO^{\odot})$ aggregates due to weak attractive forces present in the hydrocarbon chains.

- c. Due to preferential adsorption of ions from solution or due to formation of electrical double layer: Preferential adsorption of ions is the most accepted reason. The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions. When two or more ions are present in a dispersion medium, preferential adsorption of a ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:
 - i. When silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged colloidal solution results. However, when KI solution is added to AgNO₃ solution, positively charged sol results due to the adsorption of Ag[®] ions from dispersion medium.

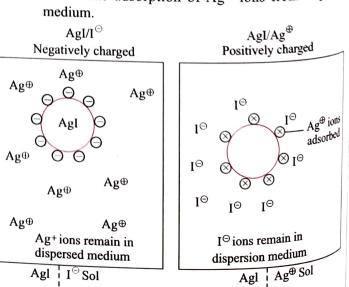


Fig. 5.23 Selective adsorption of ions

ii. If FeCl₃ is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to the adsorption of Fe³⁺ ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH[©] ions.

Fe₂O₃·xH₂O/Fe³⁺ Fe₂O₃·xH₂O/OH[©] Negatively charged

gleetrokinetic potential or zeta potential

After acquiring a positive or a negative charge by selective After acquiring on the surface of a colloidal particle, this layer attracts also from the medium forming a second layer, as shown of Fig. 5.24.

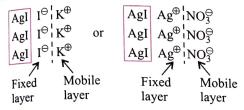


Fig 5.24 Formation of electric double layer

The combination of two layers of opposite charges around a colloidal particle is called Helmholtz electrical double layer. According to modern views, the first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed diffused layer. Since separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer result in a difference in potential between these layers. This potential difference between the fixed layer and the diffused layer of opposite charges is called the *electrokinetic* potential or zeta potential.

The presence of equal and similar charges on colloidal particles is largely responsible in providing to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another.

The electrical properties of colloidal solutions are related with two phenomena:

- i. Electrophoresis
- ii. Electro-osmosis
- i. Electrophoresis: The existence of charge on colloidal particles is determined by electrophoresis experiment. In this experiment when electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards positive or negative electrodes depending upon their charge under the influence of electric field.

The phenomenon of the movement of colloidal particles under an applied electric field is called *electrophoresis*. The positive charged particles move towards the cathode while negatively charged particles move towards the anode. Thus, by observing the direction of movement of the colloidal particles, the sign of the charged carried by the particles can be determined.

These can be demonstrated by the following experimental setup (Fig. 5.25).

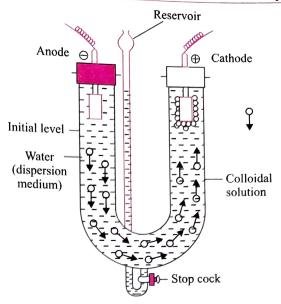


Fig. 5.25 Electrophoresis setup

ii. Electro-osmosis: Electro-osmosis may be defined as a phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric field whereas colloidal particles are not allowed to move.

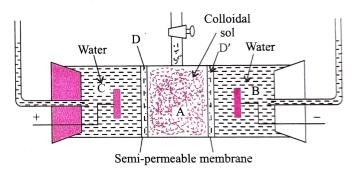


Fig. 5.26 Electro-osmosis

The electro-osmosis can be observed by a simple apparatus as shown in Fig. 5.26. The colloidal solution is placed in a compartment A separated from compartments B and C by semi-permeable membranes D and D'. The compartments B and C are filled with water up to the marks indicated by the side arms. When a potential is applied across the two electrodes placed near the membranes in B and C, the liquid level is observed to fall on one side and rise on the other side due to the passage of water through membranes D and D'. The direction of the flow of water depends on the charge of the colloid. For positively charged sols, the medium is negatively charged, and hence the flow will take place from C to B. On the other hand, for negatively charged sols, the reverse will occur and the level on the C side will rise.

5.5.5 COAGULATION OR PRECIPITATION OR FLOCCULATION OF COLLOIDS

The stability of lyophobic sols is due to the presence of charge on colloidal particles. If, somehow, the charge is removed, the particles will come nearer to each other to form aggregates

(or coagulate) and settle down under the force of gravity. The process of settling of colloidal particles is called coagulation or. precipitation of the sol. The coagulation of the lyophobic sols can be carried out in the following ways:

- a. By electrophoresis: The colloidal particles move towards oppositely charged electrodes and get discharged and precipitated.
- b. By mixing two oppositely charged sols: Oppositely charged sols when mixed in almost equal proportions, neutralize their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (-ve sol) brings them in the precipitated forms. This type of coagulation is called mutual coagulation.
- By boiling: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.
- d. By persistent dialysis: On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.
- e. By addition of electrolytes: When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralization leading to their coagulation. The ion responsible for the neutralization of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.

Hardy Schulze Rule

The coagulation capacity of different electrolytes is different. It depends upon the valency of the active ion or called flocculating ion which is an ion-carrying charge opposite to the charge on the colloidal particles. According to Hardy Schulze rule, greater the valency of the active ion or flocculating ion, greater will be its coagulating power. Thus, according to Hardy Schulze rule:

- a. The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
- b. The coagulating power of an electrolyte is directly proportional to the fourth power of the valency of the active ions (ions causing coagulation). Greater is the valency of the oppositely charged ion of the electrolyte being added, faster is the coagulation. For example, to coagulate negative sol of As_2S_3 , the coagulating power of different cations has been found to decrease in the order as:

$$Al^{3+} > Mg^{2+} > Na^{\oplus}$$

Similarly, to coagulate a positive sol such as $Fe(OH)_3$, the coagulating power of different anions has been found to decrease in the order.

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{\odot}$$

The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as coagulation value or flocculation value. It is usually expressed

as millimoles per litre. For example, the flocculating values (in as infilinoles per litre) for the coagulation of positively charged Fe(OH), millimoles per litre) for the coagulation of positively charged Fe(OH), sol and negatively charged As_2S_3 sol are given in Table 5.10. Table 5.10 Flocculating values (in millimole/litre) of common

electrolytes

Electrolyte	Active ion (anion)	Flocculating value (millimole per litre)
Férric hydroxid	e (+) sol	103
KCl	Cl [⊚] Br [⊙]	138
KBr		0.210
K ₂ SO ₄	SO_4^{2-} $C_2O_4^{2-}$	0.238
$Na_2C_2O_4$ $K_3[Fe(CN)_6]$	$C_2O_4^{2-}$ [Fe(CN) ₆] ³⁻	0.096
Arsenic sulphide	e (+) sol	
NaCl	Na [⊕]	51
KCl	K^\oplus	50
	Mg^{2+}	0.72
MgSO ₄	Ba ²⁺	0.69
BaCl ₂ AlCl ₃	Al ³⁺	0.093

Table 5.10 shows that the coagulating power is inversely proportional to coagulation value or flocculation value.

The relative coagulating powers may be compared as:

Coagulating power of electrolyte 1

Coagulating power of electrolyte 2

Coagulating value of electrolyte 2
Coagulating value of electrolyte 1

For example, for coagulation of negatively charged As₃S₃ sol

Coagulating power of AlCl₃

Coagulating power of NaCl

$$= \frac{\text{Coagulating value of NaCl}}{\text{Coagulating value of AlCl}_3} = \frac{51}{0.093} = 548$$

Thus, AlCl₃ has 548 times more coagulating power than NaCl.

ILLUSTRATION 5.39

For the coagulation of 10 mL of Fe(OH)₃ sol, 2 mL of 1 M KBr is required. What is the flocculation value of KBr?

Sol. 2 mL of 1 MKBr contains KBr = $\frac{1}{1000} \times 2 \text{ mol} = 2 \text{ mmol}$

Thus, 10 mL of Fe(OH)₃ sol requires KBr for complete coagulation = 2 mmol

.. 1 L, i.e., 1000 mL, of the sol requires KBr for complete coagulation = 200 mmol

Hence, flocculation value of KBr = 200

Coagulation of lyophilic sols congulation of the stability of the stab there are two Interest factors are the charge and solvation of the population of the population are two factors are removed. hilic sols. When these two factors are removed, a lyophilic sold he coagulated. This is done (a) by adding an old he coagulated. noted a lyophilic and solvents are removed, a lyophilic and solvents are removed, a lyophilic golcan be coagain as suitable solvent. When solvents such as alcohol and by are added to hydrophilic sols, the dehydration by adding a added to hydrophilic sols, the dehydration of dispersed active as alcohol and the source and the so actione are audition, a small quantity of electrolyte phase occurs. Under this condition, a small quantity of electrolyte in about coagulation. pnass about coagulation.

5,5,6 PROTECTION OF COLLOIDS 5.5.0 results are more stable than lyophobic sols. This is due the fact that lyophilic colloids are extensively solvated, i.e., olloidal particles are covered by a sheath of the liquid in which they are dispersed.

Lyophilic colloids have a unique property of protecting hophobic colloids. When a lyophilic sol is added to the lyophobic the lyophilic particles form a layer around lyophobic particles thus, protect the latter from electrolytes. Lyophilic colloids the for this purpose are called protective colloids.

Gold number: The lyophilic colloids differ in their protective nower. The protective power is measured in terms of gold number ad is defined as the number of milligrams of a lyophilic colloid will just prevent the precipitation of 10 mL of a gold sol on me addition of 1 mL of 10% sodium chloride solution.

The gold number of a few protective colloids is as follows:

S. No.	Protective colloid	Gold number
1.	Gelatin	0.005-0.01
2.	Haemoglobin	0.03
3.	Gum arabic	0.15
4.	Egg albumin	0.08-0.10
5.	Potato starch	25
6.	Sodium oleate	0.4
7.	Gum tragacanth	2
8.	Starch	25-50

It may be noted that smaller the value of the gold number, greater will be the protecting power of protective colloids.

Therefore, the reciprocal of gold number is a measure of the protective power of the colloid. Thus, out of the list given above, gelatin is the best protective colloid.

Congo rubin number: The protective action of a lyophilic colloid is sometimes expressed in terms of congo rubin number, as suggested by Ostwald. It is defined as the minimum amount of protective colloid in milligrams that prevent the colour change of 100 mL of 0.01% congo rubin dye to which 0.16 g equivalent of KCl is added.

ILLUSTRATION 5.40

^{On} addition of 1 mL solution of 10% NaCl to 10 mL gold sol in the presence of 0.0250 g of starch, the coagulation is just prevented. What is the gold number of starch?

Amount of starch in mg that prevent coagulation by 1 mL of 10% NaCl solution = $0.025 \times 1000 = 25$. Hence, gold number = 25.

5.5.7 COLLOIDS AROUND US

Most of the substances we come across in our daily life are colloids. The meals we eat, the clothes we wear, the wooden furniture we use, the houses we live in, the newspapers we read, are largely composed of colloids.

Following are the interesting and noteworthy examples of colloids:

- a. Blue colour of the sky: Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.
- b. Fog, mist, and rain: When a large mass of air containing dust particles is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in air in the form of mist or fog. Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositely charged clouds meet.

It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.

- c. Food articles: Milk, butter, halwa, ice-creams, fruit juices, etc., are all colloids in one form or the other.
- **d.** Blood: It is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.
- e. Soils: Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils adsorb moisture and nourishing materials.
- f. Formation of delta: River water contains charged colloidal particles of clay, sand, and many other materials. Sea water is a very big store house of a variety of electrolytes dissolved in it. As soon as river water comes in contact with sea water, the electrolytes present in sea water coagulate the suspended colloidal particles which ultimately settle down at the point of contact. Thus, the level of the river bed rises. As a result, water adopts a different course and delta is formed in due course of time (Fig. 5.27).

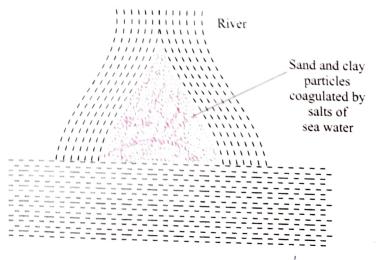


Fig. 5.27 Formation of delta

5.5.8 APPLICATIONS OF COLLOIDS

Colloids are widely used in the industry. Following are some examples:

a. Electrical precipitation of smoke: Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called Cottrell precipitator (Fig. 5.28).

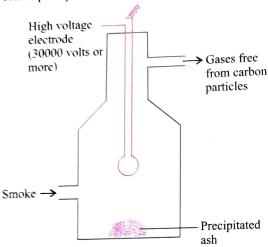


Fig. 5.28 Cottrell smoke precipitator

- b. Purification of drinking water: The water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.
- c. Medicines: Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kala azar. Colloidal gold is used for intramuscular injection. Milk of magnesia an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.
- d. Tanning: Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.
- e. Cleansing action of soaps and detergents
- f. Photographic plates and films: Photographic plates or films are prepared by coating an emulsion of the light- sensitive silver bromide in gelatin over glass plates or celluloid films.
- g. Rubber industry: Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.
- h. Industrial products: Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions.

5.6 EMULSIONS

Emulsions are colloidal solutions in which both the dispersed phase and dispersion medium are liquids. It can be defined as the dispersion of finely divided droplets in another liquid. Any t_{W_0} immiscible liquids can form an emulsion. For example, $mil_{k is a}$ naturally occurring emulsion in which the particles (or $globule_s$) of liquid fats are dispersed in water.

Emulsions are generally prepared by vigorously shaking t_{W_0} immiscible or partially miscible liquids, through a colloid mill, called the homogenizer. Generally, one of the two liquids is water.

5.6.1 Types of Emulsions

Emulsions are mainly of two types:

- a. Oil-in-water-type emulsions (O/W type): In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. For example, milk, vanishing cream, etc.
- b. Water-in-oil-type emulsions (W/O type): In this type of emulsion, water is the dispersed phase and oil is the dispersion medium. For example, butter, cod liver oil, cold cream, etc.

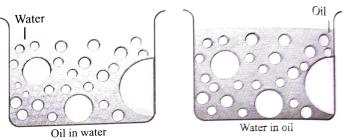


Fig. 5.29 Types of emulsions

Emulsions of oil and water are unstable and sometimes on standing they separate into two layers. For the stabilization of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agents form an interfacial film between suspended particles and the medium. The principal agents for O/W emulsions are proteins, gums. natural and synthetic soaps, etc. For W/O emulsions, the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols, lamp black, etc.

Role of an Emulsifier

The stabilization of an emulsion by means of emulsifier is called *emulsification*.

The main function of the emulsifier is to reduce the interfacial tension between the two liquids forming the emulsion. Emulsifiers are generally long-chain molecules having polar groups.

The role of an emulsifier can be explained by taking the example of soap as an emulsifier. As already studied, the soaps are sodium or potassium salts of higher fatty acids such as sodium palmitate ($C_{15}H_{31}COONa$), sodium stearate ($C_{17}H_{35}COONa$). A molecule of soap consists of two parts: hydrocarbon non-polar part (e.g., $C_{15}H_{31}$, $C_{17}H_{35}$, etc.) which is soluble in oil and the polar group ($-COO^{\circ}Na^{\oplus}$) which is soluble in water.

R—COO
$$^{\bigcirc}$$
Na $^{\oplus}$

When a drop of oil is surrounded by soap solution, R-part of the soap remains in oil and the COO[□]Na[⊕] part remains in water as shown in Fig. 5.30. As a result, soap molecules get concentrated over the surface of the drop of oil and, therefore, form protective film around each oil drop. As a result, the interfacial tension

therefore, they are intermixed therefore, they are intermixed the emulsion. be form the emulsion.

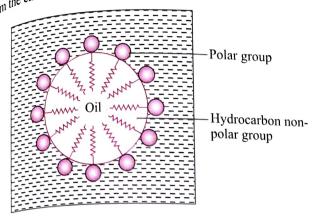


Fig 5.30 Role of soap as an emulsifier

Emulsions can be diluted with any amount of the dispersion on the other hand, the dispersed liquid when mixed forms separate layer. The droplets in emulsions are often negatively harged and can be precipitated by electrolytes. They also show Rownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

5.6.2 IDENTIFICATION OF EMULSIONS

The oil-in-water and water-in-oil emulsions can be identified by the following tests:

- a. Microscopic method: To a small amount of the given emulsion, a few drops of water are added. The water will mix completely if the emulsion is of oil-in-water type. Likewise, for the water-in-oil emulsion the miscibility with a few drops of oil can be tested. The miscibility can be seen under a microscope.
- b. Conductance method: This method is based upon adding a small amount of an electrolyte to the emulsion. If the conductance increases, the emulsion is oil-in-water type and if there is no significant change, it is water-in-oil type.
- c. Dye method: A small amount of oil-soluble dye is added to the emulsion. If it is water-in-oil type, it becomes deeply coloured, otherwise it remains colourless.

5.6.3 PROPERTIES OF EMULSIONS

Following are the characteristic properties of emulsions:

- a. Emulsions exhibit all the properties such as Tyndall effect, Brownian movement, electrophoresis, coagulation on the addition of electrolytes (containing multivalent positive ions, as the dispersed particles, i.e., globules are usually negatively charged) as shown by colloidal sols.
- b. The size of the dispersed particles in an emulsion is larger than those in the sols. It ranges from 100 Å to 10000 Å.
- c. Emulsions can be broken to yield the constituent liquid by heating, centrifuging, by adding larger amounts of the electrolytes to precipitate out the dispersed phase, or by chemical destruction of the emulsifying agent. The separation of cream from milk is a well-known example of centrifuging.

The process of breaking an emulsion to yield the constituent liquids is called demulsification.

5.6.4 APPLICATION OF EMULSIONS

Emulsions are useful in a number of way. A few of the applications are given below.

- a. In the metallurgical processes, the concentration of ore by froth floatation process is based upon the treatment of the powdered ore with oil emulsion. The valuable particles of the ore form foam which comes to the surface and is skimmed off.
- b. Asphalt emulsified in water is used for building roads without the necessity of melting the asphalt.
- c. Milk which is an important constituent of our diet is an emulsion of liquid fats in water.
- d. Several oily drugs are prepared in the form of emulsions.
- e. The cleansing action of ordinary soap for washing clothes, crockery, etc., is based upon the formation of oil-in-water emulsion.
- f. The digestion of fats in the intestine takes place by the process of emulsification. A small amount of the fat reacts with the alkaline solution present in the intestine to form a sodium soap. This soap causes the emulsification of the rest of the fat thereby making the function of the digestive enzymes easier in carrying out the metabolic processes.

5.6.5 HARMFUL EFFECTS OF EMULSIONS

The formation of emulsions is sometimes harmful. For example, petroleum forms emulsion with water. Thus, in the petroleum wells, we get an emulsion sometimes instead of petroleum alone. Likewise, in the area where small amounts of petroleum are present, the well water becomes unfit for use.

5.7 GELS

A gel is a colloidal system in which a liquid is dispersed in a solid. Under certain conditions, the lyophilic sols may be coagulated to give a semi-solid jelly-like mass which encloses all the liquid present in the sol. The process of gel formation is called gelation and the colloidal system formed is called gel. The common examples of gel are: gum arabic, gelatin, processed cheese, silicic acid, ferric hydroxide, etc.

Gels are formed by the interlocking of the particles of solid dispersion medium in the form of a loose framework inside which liquid (dispersed phase) is contained.

When the gel is allowed to stand for a long time, it shrinks and loses the entire liquid held by it. This shrinking of gel is termed as syneresis or weeping.

Gels may be classified into two types:

- a. Elastic gels
- b. Non-elastic gels

The main points of difference between the two are as follows:

Elastic gels

- a. Gels which possess the property of elasticity, i.e., they change to dehydratic solid mass which can again be converted into gel by addition of water followed by heating and cooling.
- b. When placed in contact with water they absorb water and swell. This property is called imbibition.
- c. Examples include gelatin, agar-agar, starch, etc.

Non-elastic gels

- a. Gels which do not possess the property of elasticity, i.e., they change into solid mass on dehydration which becomes rigid and cannot be converted into the original form by heating with water.
- **b.** They do not show the phenomenon of imbibition.
- c. Most common example is silicic acid.

Thixotropy: Some gels, such as gelatin, on mechanical shaking lose their semi-solid gel-like character and change into a liquid sol. This sol on standing again changes into gel. This phenomenon is known as thixotropy.

5.7.1 LYOTROPIC SERIES OR HOFMEISTER SERIES

When a gel is placed in a suitable liquid, it absorbs a large volume of the liquid. The phenomenon is called imbibition or swelling. The effect of the presence of salts on swelling was studied by Hofmeister (1891). He found that for the salts of the same cation (e.g. Na[®]) the effect of certain other anions was to inhibit the imbibition while that of certain other anions was to favour the imbibition. For example in case of iodides, the swelling is so high that the gel disperses into sol even at room temperature. In other cases, the sol is formed by warming the swollen gel. The order of the temperature to which the gel must be heated in the presence of various anions, before it changes into sol in called Hofmeister series or lyotropic series. The order is:

Citrate³⁻ > Tartarate²⁻ > SO_4^{2-} > PO_4^{3-} > Acetate > Cl^{\odot} > NO_3^{\odot} $> Br^{\ominus} > I^{\ominus} > CNS^{\ominus}$.

The anions from citrate to acetate inhibit the imbibition while from Cl[⊕] to CNS[⊕] favour the imbibition.

ILLUSTRATION 5.41

What are micelles? How do they differ from ordinary colloidal particles? Give two examples of micelles-forming substances.

Sol. There are some substances which at low concentration behave as normal electrolyte but at higher concentrations exhibit colloidal behaviour due to the formation of aggregated particles. The aggregated particles thus formed are called micelles.

The formation of micelles takes place only above a particular temperature called Kraft temperature and above a particular concentration called critical micellization concentration (CMC). On dilution these colloids revert back to individual ions.

Examples are soaps and synthetic detergents.

ILLUSTRATION 5.42

State Hardy Schulze rule.

Sol. Greater the valency of the action ion of the electrolyte greater will be its precipitating action.

 $AI^{3+} > Mg^{2+} > Na^{\oplus}$ for negatively charged sols $PO_4^{3-} > SO_4^{2-} > Cl^{\odot}$ for positively charged sols

ILLUSTRATION 5.43

Describe the following types of colloids, giving an example for each:

- a. Multimolecular colloids
- b. Macromolecular colloids

Sol.

- a. Multimolecular colloids: A large number of atoms or smaller molecules of a substance on dissolution aggregate together to form species having size (diameter < 1 nm) in the colloidal range (1-1000 nm). Such species are. known as multimolecular colloids. For example, a sulphur sol consist of particles containing a thousand or more $\mathbb{S}_{\scriptscriptstyle{o}}$ sulphur molecules.
- b. Macromolecular colloids: Macromolecules (starch, cellulose, proteins and nylon, polyethene, etc.) when dissolved in suitable solvent form a solution wherein the size of the macromolecule may fall within the colloidal range. Such systems are called macromolecular colloids.

ILLUSTRATION 5.44

What is Kraft temperature?

Sol. Kraft temperature is the minimum temperature above which the formation of miscelles takes place.

ILLUSTRATION 5.45

What is meant by the term peptization?

Sol. The process of conversion of a freshly prepared precipitate into a colloidal solution by adding a suitable electrolyte is called peptization.

ILLUSTRATION 5.46

Which one of the following electrolytes is most effective for the coagulation of Fe(OH)₃ sol and why?

Sol. Fe(OH)₃ is a positively charged sol. According to Hardy Schulze rule, greater the charge on an oppositely charged ion of the electrolyte added, more effective it is in bringing about the coagulation. Hence, Na₃PO₄ (containing PO₄) ions) is most effective.

ILLUSTRATION 5.47

How is dialysis carried out? Mention its one application.

Dialysis is used for purification of colloidal solution.

It is carried out by putting impure colloidal solution in a parchment paper bag and then dipping it in distilled water. After some time, the molecules and ions diffuse through the after some into the water leaving the pure colloidal solution membrane into the water leaving the pure colloidal solution hehind. An important application of dialysis is during the purification of blood in the artificial kidney machine.

ILLUSTRATION 5.48

For the coagulation of 100 mL of arsenious sulphite sol, 5 mL of NaCl is required. What is the flocculation value of NaCl?

 $_{5 \text{mL of 1 M NaCl contains NaCl}} = \frac{1}{1000} \times 5 \text{ mol} = 5 \text{ mmol}$ Thus, 100 mL of As₂S₃ sol require NaCl for complete coagulation = 5 mmol

11 L, i.e., 1000 mL of the sol requires NaCl for complete, coagulation = 50 mmol

Therefore, the flocculation value of NaCl = 50

ILLUSTRATION 5.49

The coagulation of 200 mL of a positive colloid took place when 173 g HCl was added to it without changing the volume much. The floculation value of HCl for the colloid is

a. 36.5

b. 100

c. 200

d. 150



b. 200 mL of the sol requires = 0.73 g HCl

Moles of HCl = $\frac{0.73}{36.5}$ mol = 0.02 mol = 20.0 mmol

Therefore, 1000 mL (1 L) of the sol will require

 $= \frac{20}{200} \times 1000 = 100 \text{ mmol}$

LLUSTRATION 5.50

What is observed when sodium chloride is added to a colloidal solution of ferric hydroxide?

When sodium chloride is added to ferric hydroxide solution, the solution gets coagulated. This is because Cl^o ions from NaCl neutralize the +ve charge on Fe(OH)₃ solution.

ILLUSTRATION 5.51

Give two examples of colloidal solutions of liquid dispersed in solid. What is the name of the colloidal solution?

Jelly, cheese. The name of these colloidal solutions is gel.

ILLUSTRATION 5.52

The coagulation of 100 mL of a colloidal Solution of gold is completely prevented by the addition of 0.30 g of starch to it before adding 1 mL of 10% NaCl solution. Find out the gold number of starch?

Sol. Starch added to 100 mL of gold sol to completely prevent coagulation by 1 mL of 10% NaCl sol = 0.30 g = 300 mg Starch required to be added to 10 mL of gold sol to completely prevent coagulation by 1 mL of 10% NaCl sol = 30 mg

Therefore, by definition, gold number of starch = 30

ILLUSTRATION 5.53

50 mL of standard gold solution needs 0.05 mg of gelatin for its protection from coagulation. Calculate the gold number of gelatine?

Sol. 50 mL of standard gold sol requires = 0.05 mg of gelatin Therefore, 10 mL of standard gold sol requires

$$=\frac{0.05}{50} \times 10 = 0.01$$
 mg of gelatine

 \therefore Gold number = 0.01

ILLUSTRATION 5.54

Explain the following observations:

- a. Lyophilic colloid is more stable than lyophobic colloid.
- **b.** Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.
- c. Sky appears blue in colour.

Sol.

- a. It is due to the greater force of attraction between dispersed phase and dispersion medium in lyophilic colloid than lyophobic colloid.
- b. Fe(OH)₃ sol is positively charged which is coagulated by negatively charged Cl[©] present in sodium chloride solution.
- c. Sky appears blue in colour due to the scattering of light by colloidal particles. This is known as Tyndall effect.

ILLUSTRATION 5.55

What is the difference between a colloidal solution, gel, and emulsion?

Sol. In a colloidal sol, the dispersed phase is a solid and the dispersion medium is a liquid. In a gel, it is just the opposite. In an emulsion, both the dispersed phase and dispersion medium are liquids.

ILLUSTRATION 5.56

What type of colloidal sols are formed in the following:

- a. Sulphur vapours are passed through cooled water.
- b. White of an egg is mixed with water.
- c. Soap solution.

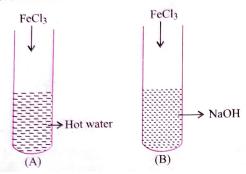
Sol.

- a. Multimolecular because sulphur molecules associate together to form colloidal sol.
- **b.** *Macromolecular* because protein molecules present in the white of the egg are macromolecules soluble in water.
- c. Associated because RCOO[©] ions associate together to form micelles.

ILLUSTRATION 5.57

A colloidal solution of ferric oxide is prepared by two different methods as shown below.

- a. What is the charge on colloidal particles in the two test tubes (A) and (B)?
- b. Give reasons for the origin of charge.



Sol.

- **a.** Colloidal particles of test tube (A) are positively charged where as colloidal particles of test tube (B) are negatively charged.
- **b.** In test tube (A), Fe^{3+} is adsorbed on the precipitate Fe_2O_3 : xH_2O [or Fe_2O_3 : xH_2O/Fe^{3+} is formed].

In test tube (B), $\stackrel{\odot}{OH}$ ion is adsorbed on the precipitate $Fe_2O_3\cdot xH_2O$ [or $Fe_2O_3\cdot xH_2O/\stackrel{\odot}{OH}$ is formed].

ILLUSTRATION 5.58

Explain the following observations:

- **a.** A beam of light passing through a colloidal solution has a visible path.
- **b.** Passing an electric current through a colloidal solution removes colloidal particles from it.
- c. Ferric hydroxide sol coagulates on addition of potassium sulphate.

Sol.

- a. This is due to scattering of light by the colloidal particles (called Tyndall effect).
- **b.** This is due to charge on the colloidal particles so that they migrate towards the oppositely charged electrode.
- c. Ferric hydroxide is a positively charged sol and is coagulated by SO_4^{2-} ions produced by K_2SO_4 .

ILLUSTRATION 5,59

Compare the coagulation power of AlCl₃ with that of NaCl. Given that their coagulation values are 0.093 and 52 respectively.

Sol. As coagulation power is inversely proportional to coagulation value, the ratio of their coagulation power will be

Coagulation power of AlCl₃
Coagulation power of NaCl

$$= \frac{\text{Coagulation value of NaCl}}{\text{Coagulation value of AlCl}_3} = \frac{52}{0.093} = 559$$

Thus, $AlCl_3$ has 559 times greater coagulation power than NaCl.

ILLUSTRATION 5.60

Compare the coagulating power of HCl with that of KBr. Given the coagulation values are 30.8 and 138, respectively?

Sol. The coagulation power is inversely proportional to the coagulation value, the ratio of their coagulation power is Coagulation power of HCl

Coagulation power of KBr

$$= \frac{\text{Coagulation value of KBr}}{\text{Coagulation value of HCl}} = \frac{138}{30.8} = 4.48$$

Thus, HCl has 4.48 times greater coagulation power than KBr.

ILLUSTRATION 5.61

What modification can you suggest in the Hardy Schulze law?

Sol. According to the Hardy Schulze law, the coagulation ion has charge opposite to that on the colloidal particles. Hence, the charge on colloidal particles is neutralized and coagulation occurs. The law can be modified to include the following:

When appositely charged sols are mixed in proper

When oppositely charged sols are mixed in proper proportions to neutralize the charges of each other, coagulation of both the sols occurs.

ILLUSTRATION 5.62

Why is it essential to wash the precipitate with water before estimating it quantitatively?

Sol. Some amount of the electrolytes mixed to form the precipitate remain adsorbed on the surface of the particles of the precipitate. Hence, it is essential to wash the precipitate with water to remove the sticking electrolytes (or any other impurities) before estimating it quantitatively.

ILLUSTRATION 5.63

What is meant by critical micellization concentration?

Sol. The micelle may be defined as the aggregated particles formed by associated colloids in solution. The formation of micelles takes place above certain concentration called critical micellization concentration (CMC). Every micelle system has a specific value of CMC.

ILLUSTRATION 5.64

What type of substances form lyophobic sols?

Sol. Substances such as metals, their sulphides, etc., which do not mix directly with the dispersion medium form a lyophobic sol.

ILLUSTRATION 5.65

Define emulsification? The process of making an emulsion from an oil is termed as emulsification. as emulsification.

ILUSTRATION 5.66

Gelatin is generally added to ice creams. Why?

Ice cream is an emulsion of milk or cream in water, i.e., oil-in-water type. Gelatin is added to act as an emulsifier, i.e., it helps to stabilize the emulsion.

ILLUSTRATION 5.67

What is the significance of reciprocal of "gold number"?

Smaller the gold number, greater is its protective power. Hence, the reciprocal of gold number is a direct measure of the protective power of the colloid.

ILLUSTRATION 5.68

What is common in aqua sols and solid aerosols? How do they differ?

Aquasol and solid aerosol both have solid as the dispersed phase. They differ in dispersion medium. Aquasols have water as the dispersion medium, while aerosols have gas as the dispersion medium.

ILLUSTRATION 5,69

What is colloidion?

Colloidion is cellulose nitrate peptized by ethanol.

ILLUSTRATION 5.70

Define colloidal solution?

M. A colloidal solution is a state in which the particle size lies between 1 nm and 100 nm. It appears to be homogeneous but actually it is heterogeneous.

ILLUSTRATION 5.71

A sol of AgI can be positively or negatively charged. Explain how and why?

Charge on the colloidal particles is due to the preferential adsorption of common ions. AgI on shaking with excess of KI adsorbs negative I ions and hence is negatively charged. However, on shaking AgI with excess of AgNO₃ solution, it will adsorb Ag^{\oplus} ions and hence becomes positively charged.

ILLUSTRATION 5.72

Give four uses of emulsion.

- a. The concentration of sulphide ore by froth flotation process is based on emulsification.
- b. Phenyl, used as disinfectant, is an emulsion of oil in water.

- c. Milk is an emulsion of fat in water.
- d. Butter is an emulsion of water dispersed in fat

ILLUSTRATION 5.73

Give an example of an associated colloid?

Sol. Soaps and detergents are associated colloids.

ILLUSTRATION 5.74

Give one example of positively charged sol and one example of negatively charged sol.

Sol. Fe(OH)₃ is a positively charged sol whereas As_2S_3 is a negatively charged sol.

ILLUSTRATION 5.75

What is electrodialysis?

Sol. It is a process by which colloidal solutions containing ionic impurities are purified. The colloidal solution containing ionic impurities is placed in a bag of parchment paper in distilled water electric field. The ions come out through parchment paper and the sol is purified.

ILLUSTRATION 5.76

What is the main cause of charge on a colloidal solution?

Sol. The charge on the colloidal particles is due to the adsorption of common ions of the electrolyte on the surface of the colloidal particles, e.g., Fe3+ from FeCl3 on the surface of Fe(OH), particles.

ILLUSTRATION 5.77

Why do colloidal solutions exhibit Tyndall effect?

Sol. Colloidal solutions exhibit Tyndall effect because the size of the colloidal particles (10-1000 Å) is such that they can scatter light.

ILLUSTRATION 5.78

Define ultrafiltration.

Sol. In this process, colloidal solutions are purified by carrying out filtration through special types of graded filters called ultra-filters. Filter paper allows the passage of electrolyte but does not allow the passage of colloidal particles.

ILLUSTRATION 5.79

Which is not the characteristic of hydro-phobic sols?

- a. They are highly susceptible to coagulation by addition of
- b. They have nearly the same surface tension and viscosity as that of dispersion medium.
- c. Their stability is due to both electric charge and salvation
- d. Sol particles can be seen under ultramicroscope.

Sol.

c. The stability is attributed to electric charge on the sol particles.

ILLUSTRATION 5.80

Hydrophilic gels, when placed in water, absorb liquid resulting in an increase of their volume. This process of swelling of gels takes place with

- a. No change in volume
- b. Net increase in volume
- c. Net decrease in volume
- d. Large reduction in volume

Sol. c. There will be net decrease in volume.

ILLUSTRATION 5.81

Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl, Na₂SO₄, and Na₃PO₄ solutions. Their coagulating values will be in the order

- $a. NaCl > Na_2SO_4 > Na_3PO_4$
- b. Na₂SO₄ > Na₃PO₄ > NaCl
- c. $Na_3PO_4 > Na_2SO_4 > NaCl$
- **d.** $Na_2SO_4 > NaCl > Na_3PO_4$

Sol.

a. Since the sol particles migrate toward cathode, they are positively charged. Hence, anions would be effective in coagulation. Greater is the valence of effective ion, smaller will be its coagulation value.

ILLUSTRATION 5.82

During electro-osmosis of Fe(OH)₃ sol

- a. Sol particles move towards anode
- b. Sol particles move towards cathode
- c. The dispersion medium move towards anode
- d. The sol particles do not move in either direction

Sol.

(c, d) In electro-osmosis, the sol particle are prevented from migration where as the dispersion medium migrates in the direction opposite to those of particles. Here the medium is negatively charged.

ILLUSTRATION 5.83

Which of the following ionic substances will be most effective in precipitating the sulphur sol?

a. KCl

- b. BaCl₂
- c. Fe₂(SO₄)₃
- d. Na₃PO₄

Sol.

c. The sulphor sol is negatively charged and would be coagulated most effectively by Al³⁺.

ILLUSTRATION 5.84

The colligative property of a sol compared to the aqueous solution of glucose of same concentration will be

- a. Much smaller
- b. Much higher
- c. The same
- d. Slightly lower

Sol.

 Molar concentration of a sol is much smaller than that in a true solution of same strength (g L⁻¹) due to much larger particles.

ILLUSTRATION 5.85

Electrolytes can cause coagulation as well as peptization of colloidal solution. Explain?

cause coagulation of colloidal solution. Electrolytes can cause peptization also, e.g., FeCl₃ can peptize Fe(OH)₃ precipitate because it gives excess of Fe³⁺ ions which get adsorbed on Fe(OH)₃ precipitates. This breaks up the precipitate into smaller particles of the size of colloid.

CONCEPT APPLICATION EXERCISE 5.2

- 1. What are enzymes? Write brief mechanism of enzyme catalysis?
- 2. Give the general method of preparation of sols.
- 3. Describe the methods for the purification of colloidal solution.
- 4. Describe the electrical properties of colloidal solution.
- 5. What is emulsion? Write its applications.
- 6. What is demulsification?
- 7. Describe the cleansing action of soap.
- 8. How are associated colloids different from macromolecular and multimolecular colloids?
- 9. How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?

Solved Examples

EXAMPLE 5.1

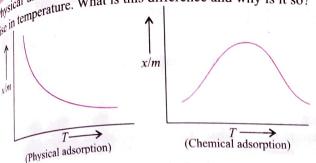
Write two differences between multi-molecular colloids and macromolecular colloids?

Sol.

- a. Multimolecular colloids are formed by the aggregation of small molecules (diameter < 1 nm) while macromolecular colloids are formed by macromolecules (polymers) and consist of single molecules.
- b. Multimolecular colloids are generally lyophobic whereas macromolecular colloids are generally lyophilic.

EXAMPLE 5.2

[NSical and chemical adsorption respond differently with a physical additional additio



Adsorption isobar for physical adsorption shows that the extent of adsorption decreases with the increase in temperature. The adsorption isobar of chemical adsorption shows that the extent of adsorption first increases and then decreases with the increase in temperature. The initial unexpected increase in the extent of adsorption with temperature is due to the fact that the heat supplied acts as the activating energy required for chemical adsorption which is much more than that of physical adsorption.

EXAMPLE 5.3

A small amount of silica gel and anhydrous calcium chloride are placed separately in two corners of a vessel containing water vapour. What phenomena will occur?

Adsorption of water will occur on silica gel and absorption of water will occur on calcium chloride.

EXAMPLE 5.4

How is adsorption of a gas related to its critical temperature?

Higher is the critical temperature of the gas, greater is the ease of liquefaction, i.e., the greater are the van der Waals forces of attraction and, hence, larger adsorption will occur.

EXAMPLE 5.5

Why are lyophilic colloidal sols more stable than lyophobic colloidal sols?

The lyophilic colloidal sols are more stable because they are highly hydrated in solution.

EXAMPLE 5.6

Give one test to distinguish whether the given emulsion is oilin-water-type or water-in-oil-type emulsion.

It can be identified by dilution test. In this method, the emulsion is diluted with water. If the emulsion gets diluted with water, this means that water acts as the dispersion medium and it is an example of oil-in-water emulsion. If it is not diluted than oil acts as the dispersion medium and it is an example of water-in-oil emulsion.

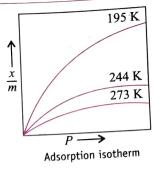
EXAMPLE 5.7

Consider the adsorption isotherm given below and interpret the variation in the extent of adsorption (x/m) when

- a. Temperature increased at constant pressure.
- b. Pressure increases at constant temperature.

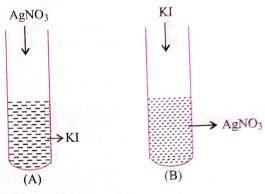
Sol.

- a. At constant pressure, adsorption decreases with increase in temperature as it is an exothermic process.
- b. As pressure increases at constant temperature, initially adsorption increases upto a particular pressure and then it remains constant.



EXAMPLE 5.8

A colloidal solution of AgI is prepared by two different methods as shown in the figure below:



- a. What is the charge of Agl colloidal particles in the two test tubes (A) and (B)?
- b. Give reasons for the origin of charge.

Sol.

- a. Test-tube (A) has negative charge whereas test tube (B) has positive charge on the colloidal particles.
- **b.** In test tube (A), I^{\odot} is adsorbed on precipitate AgI [or AgI/ I^{\odot} is formed]. In test tube (B), Ag^{\oplus} is adsorbed on precipitate AgI [or AgI/Ag $^{\oplus}$ is formed].

EXAMPLE 5.9

What role does adsorption play in hetero-geneous catalysis?

gaseous whereas catalyst is a solid. The reactant molecules are adsorbed on the surface of the solid catalyst by physical adsorption or chemisorption. As a result, the concentration of the reactant molecules on the surface increases and hence the rate of reaction increases. Alternatively, one of the reactant molecules undergoes fragmentation on the surface of the solid catalyst producing active species which react faster. The product molecules in either case have no affinity for the solid catalyst and are desorbed making the surface free for fresh adsorption. This theory is called adsorption theory.

EXAMPLE 5.10

Why is adsorption always exothermic?

Sol. When a gas is adsorbed on the surface of a solid, its entropy decreases, i.e., ΔS is negative. Now, $\Delta G = \Delta H - T \Delta S$ and for the process to be spontaneous, free energy change, ΔG must be negative.

 $T \Delta S$ is negative, i.e., $-T \Delta S$ is +ve, therefore, ΔG can be negative only if ΔH is negative. Hence, adsorption is always exothermic.

EXAMPLE 5.11

In a coagulation experiment, 5 mL of As_2S_3 is mixed with distilled water and 0.1 M solution of an electrolyte AB so that the total volume is 10 mL. It was found that all solutions containing more than 4.6 mL of AB coagulate within 5 min. What is the flocculation value of AB for As_2S_3 solution?

Sol. A minimum of 4.6 mL of AB is required to coagulate the solution. The moles of AB in the sol is

$$= \frac{4.6 \times 0.1}{10} = 0.046 \text{ mol}$$

This means that a minimum of 0.046 mol or $0.046 \times 1000 = 46$ mmol are required for coagulating 1 L of solution.

Flocculation value of AB for As_2S_3 sol = 46

EXAMPLE 5.12

In an adsorption experiment, a graph between $\log (x/m)$ versus $\log P$ was found to be linear with a slope of 45°. The intercept on the $\log (x/m)$ axis was found to be 0.3010. Calculate the amount of the gas adsorbed per gram of charcoal under a pressure of 0.5 atm.

Sol. According to the Freundlich equation

$$\frac{x}{m} = KP^{1/n}$$
or $\log \frac{x}{m} = \log K + \frac{1}{n} \log P$

∴ Plot of $\log \frac{x}{m}$ versus $\log P$ is linear with slope = $\frac{1}{n}$ and intercept = $\log K$

Thus,
$$\frac{1}{n} = \tan \theta = \tan 45^\circ = 1$$
 or $n = 1$.

 $\log K = 0.3010$ or K = antilog 0.3010 = 2. At P = 0.5 atm

$$\frac{x}{m} = KP^{1/n} = 2 \times (0.5)^1 = 1.0$$

EXAMPLE 5.13

The volume of nitrogen gas Vm (at STP) required to cover a sample of silica gel with a mono-molecular layer is $129 \text{ cm}^3\text{g}^{-1}$ of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies $16.23 \times 10^{-20} \text{ m}^2$.

Sol. $22400 \text{ cm}^3 \text{ of N}_2 \text{ at STP contain} = 6.023 \times 10^{23} \text{ molecules}$ $\therefore 129 \text{ cm}^3 \text{ of N}_2 \text{ at STP will contain}$

$$= \frac{6.023 \times 10^{23} \times 129}{22400} = 3.468 \times 10^{21} \text{ molecules}$$

Area occupied by a single molecule = $16.2 \times 10^{-20} \text{ m}^2$

Therefore, area occupied by 3.468×10^{21} molecules of N_2 = $(16.2 \times 10^{-20}) \times (3.468 \times 10^{21})$ m² = 561.8 m²

Therefore, surface area per gram of gel = 561.8 m^2

EXAMPLE 5.14

100 mL of a colloidal solution is completely precipitated by addition of 5 mL of 1 M NaCl solution. Calculate the coagulation value of NaCl.

Sol. Coagulation value is the millimoles of an electrolyte that must be added to 1 L of a colloidal solution for complete coagulation.

∴ 5 mL of 1 M NaCl =
$$\frac{1}{1000}$$
 × 5 = 0.005 mol or 5 mmol

100 mL of a colloidal solution require NaCl for complete coagulation = 5 mmol.

Therefore, 1 L of colloidal solution require NaCl f_{0r} complete coagulation = 50 mmol

Therefore, coagulation value of NaCl = 50

EXAMPLE 5.15

What is the charge on the colloidal particles in the following?

- a. Fe(OH)₃ sol
- **b.** As_2S_3 sol
- c. Colloidal sol of silver

Sol.

- a. Fe(OH)₃ sol: +ve
- **b.** As_2S_3 sol: -ve
- **c.** Colloidal sol of silver: –ve

EXAMPLE 5.16

Which of the following is most effective in coagulating ferric hydroxide sol?

a. KC1

- b. FeCl₃
- c. Na₂SO₄
- **d.** $K_3[Fe(CN)_6]$

Sol. Since Fe(OH)₃ sol is positively charged, the anion having highest charge will be the most effective, i.e., [Fe(CN)₆]³.

EXAMPLE 5.17

Write a mathematical expression showing relationship between the amount of solute adsorbed per unit mass of the solid adsorbent and the concentration of the solute in the solution.

Sol.
$$\frac{x}{m} = K(C)^{1/n}$$
,

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C$$

where x/m is the extent of adsorption, x is the mass of adsorbate, m is the the mass of adsorbent, C is the concentration of solute in solution, and K is the constant.

CXAMPLE 5.18 EXAMPLE of chemisorption, why does adsorption first increase therease? m then decrease?

The initial increase is due to the fact that the heat The man activation energy. The decrease supplied significant states and supplied supplied significant states and supplied su _{equilibrium}.

EXAMPLE 5.19

sale one difference between physisorption and chemisorption.

There are weak van der Waals force of attraction between adsorbent and adsorbate in physisorption. It is non-specific and reversible. Chemisorption involves strong forces of chemical nature. It is highly specific and irreversible in nature.

EXAMPLE 5.20

what happens when a freshly precipitated Fe(OH)3 is shaken mit little amount of dilute solution of FeCl,?

A reddish brown colloidal solution of Fe(OH), is obtained. This process is called peptization. The Fe³⁺ ions from FeCl₃ are adsorbed on the surface of the precipitate and form positively charged colloidal solution.

$$FeCl_{3} \longrightarrow Fe^{3+} + 3Cl^{\odot}$$

$$Fe(OH)_{3} + Fe^{3+} \longrightarrow [Fe(OH)_{3}]Fe^{3+} + 3Cl^{\odot}$$
Colloidal solution

CONCEPT APPLICATION EXERCISE 5.3

- 1. What happens when persistant dialysis of colloidal solution is carried out?
- 2. What type of building blocks are present in the structure of zeolites? What is this structure called?
- 3. What do x and m represent in the following expression? $(x/m) = KP^{1/n}$
- 4. Indicate a chemical reaction involving a homogeneous catalyst.
- 5. What type of substances form lyophobic sols?
- 6. How can we remove moisture from glass apparatus?
- 7. How is adsorption of a gas related to its critical temperature?
- 8. What are the different thermodynamical parameters that illustrate the mechanism of Adsorption?
- 9. Draw the following graphs. Do mention their slope and intercept, if can be calculated?

a.
$$x/m$$
 vs p

b.
$$\log \frac{x}{m}$$
 vs $\log p$

- c. Physisorption isobar
- d. Chemisorption isobar
- 10. How does a solid catalyst enhance the rate of combination of gaseous molecule?
- 11. What is the role of diffusion in heterogeneous catalyst?
- 12. For soaps critical micelle concentration (CMC) is 10^{-x} (min.) to 10^{-y} (max.) mol/L. What is the value of x?
- 13. Twenty percent of the surface sites of a catalyst is occupied by nitrogen molecules. The density of surface sites is 6.023×10^{14} cm⁻². The total surface area is 1000 cm². The catalyst is heated to 300 K and nitrogen is completely desorbed into a pressure of 0.001 atm and volume of 2.46 cm³. Calculate the number of sites occupied by nitrogen molecules.
- 14. One gram of charcoal adsorbs 100 ml of 0.5 M acetic acid to form a monolayer, and the molarity of acetic acid reduces to 0.49. Calculate the surface area of charcoal adsorbed by each molecule of acetic acid. The surface area of charcoal is $3.01 \times 10^2 \text{ m}^2 \text{ g}^{-1}$.

ANSWERS

14.
$$5 \times 10^{19} \text{ m}^2$$

Exercises

Single Correct Answer Type

Adsorption

- 1. The effect of pressure on adsorption is high if
 - (1) Temperature is low
 - (2) Temperature is high
 - (3) Temperature is neither very low nor very high
 - (4) Charcoal piece is taken in place of charcoal powder
- 2. Which one of the following statements is wrong?
 - (1) Physical adsorption of a gas is directly related to its critical temperature.
 - (2) Chemical adsorption decreases regularly as the temperature is increased.
 - (3) Adsorption is an exothermic process.
 - (4) A solid with a rough surface is a better adsorbent than the same solid with a smooth surface.
- 3. Which of the following is true during adsorption?
 - (1) ΔG , ΔH , and ΔS all are negative.
 - (2) ΔG is negative, but ΔH and ΔS are positive.
 - (3) ΔG and ΔH are negative, but ΔS is positive.
 - (4) ΔG and ΔS are negative, but ΔH is positive.
- 4. Which one of the following statements is wrong about adsorption?
 - (1) It is a selective and specific process.
 - (2) It is a reversible process.
 - (3) An increase in the gaseous adsorbate causes an increase in a adsorption. However, at high pressure, the adsorption becomes constant.
 - (4) It is an endothermic process.
- 5. Adsorption is the phenomenon in which substance
 - (1) Accumulates on the surface of the other substance
 - (2) Goes into the body of the other substance
 - (3) Remains close to the other substance
 - (4) None is correct
- 6. Sorption is the term used when
 - (1) Adsorption takes place
 - (2) Absorption takes place
 - (3) Both take place
 - (4) Desorption takes place
- 7. In the adsorption of oxalic acid on activated charcoal, the activated charcoal is called
 - (1) Adsorbent
- (2) Adsorbate
- (3) Adsorber
- (4) Absorber
- 8. There is desorption of physical adsorption when
 - (1) Temperature is increased
 - (2) Temperature is decreased
 - (3) Pressure is increased
 - (4) Concentration is increased

- 9. The rate of chemisorption:
 - (1) Decreases with increase of pressure
 - (2) Increases with increase of pressure
 - (3) Is independent of pressure
 - (4) Is independent of temperature
- 10. Which of the following is not a characteristic of chemisorption?
 - (1) It is irreversible.
 - (2) It is specific.
 - (3) It is multilayer phenomenon.
 - (4) Heat of adsorption is about -400 kJ.
- 11. Chromatography is a technique based on
 - (1) Adsorption and then dispersion of solute
 - (2) Absorption of solute
 - (3) Hydration of solute
 - (4) Evaporation of solute
- 12. Amount of gas adsorbed per gram of adsorbent increases with pressure, but after a certain limit is reached, adsorption becomes constant. It is where
 - (1) Multilayers are formed
 - (2) Desorption takes place
 - (3) Temperature is increased
 - (4) Adsorption also starts
- 13. Softening of hard water is done using sodium aluminium silicate (zeolite). This causes
 - (1) Adsorption of Ca2+ and Mg2+ ions of hard water replacing Na[⊕] ions.
 - (2) Adsorption of Ca2+ and Mg2+ ions of hard water replacing Al³⁺ ions.
 - (3) Both (1) and (2) are true
 - (4) None is true
- 14. Which of the following is/are true statements?
 - (1) Water vapour is absorbed by anhydrous calcium chloride both adsorbed by silica gel.
 - (2) NH3 is absorbed by water but adsorbed by charcoal.
 - (3) Sugar is decolourized by animal charcoal based on adsorption.
 - (4) Water is absorbed by conc H₂SO₄.
- 15. Anionic surfactants are
 - (1) C₁₅H₃₁COONa
- SO₃Na (2) R-
- $(3) C_{18}H_{37}NH_3CI$
- (4) All
- 16. Cationic surfactants are
 - (1) C₁₇H₃₅COONa
- (3) $C_{16}H_{33}$ \sim N-Cl (4) $C_{16}H_{33}N(CH_3)_3Cl$

17. Non-ionogenic surfactants are (1) R \longrightarrow SO_3Na

(2) C₁₇H₃₅COONa

 $_{(3)}C_{n}H_{2n+1}(OCH_{2}CH_{2})_{x}OH$

Freumund of mg) at constant temperature can be expressed as

$$(1) \log \frac{X}{m} = \log P + \frac{1}{n} \log K$$

$$(2) \log \frac{X}{m} = \log K + \frac{1}{n} \log P$$

 $(3) \frac{X}{n} \propto P^n$

$$(4) \frac{X}{m} = \log P + \frac{1}{n} \log K$$

- 19. Which of the following statements is incorrect regarding physisorption?
 - (1) It occurs because of van der Waals forces.
 - (2) Liquefiable gases are adsorbed more easily.
 - (3) Under high pressure it results surface.
 - (4) Enthalpy of adsorption ($\Delta H_{\rm adsorption}$) is low and positive.
- 10. The equation of Langmuir adsorption isotherm under high pressure is:

 $(1) \ \frac{x}{m} = \frac{a}{b}$

$$(2) \frac{x}{m} = \frac{1}{ap}$$

(3) $\frac{x}{m} = \frac{b}{a}$

$$(4) \ \frac{x}{m} = ap$$

- 21. Which of the following is a wrong form of Langmuir adsorption isotherm?
 - (1) $\frac{x}{m} = \frac{a}{b}$ (At high pressure)
 - (2) $\frac{x}{m} = \frac{ap}{b}$ (At high pressure)
 - (3) $\frac{x}{m} = ap$ (At very low pressure)
 - (4) $\frac{x}{m} = \frac{b}{a} + \frac{1}{ap}$ (At intermediate pressure)
- \mathfrak{V} . For adsorption of a gas on a solid, the plot of $\log \left(\frac{x}{m} \right)$ vs

 $\log p$ is linear with slope equal to (*n* being whole number):

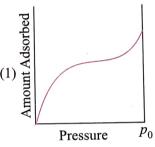
- $(1) \log k$
- (2) k

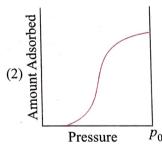
 $(3)_{n}$

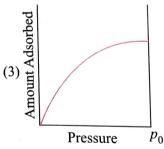
- $(4) \frac{1}{n}$
- 23. 2.0 g of charcoal is placed in 100 mL of 0.05 M CH₃COOH to form an adsorbed mono-acidic layer of acetic acid

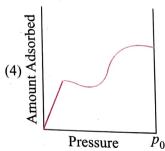
molecules and thereby the molarity of CH3COOH reduces to 0.49. The surface area of charcoal is 3×10^2 m² g⁻¹. The surface area of charcoal adsorbed by each mlecule of acetic acid is:

- (1) 1.0×10^{-19} cm²
- (2) $1.0 \times 10^{13} \text{ cm}^2$
- (3) 1.0×10^{-18} cm²
- (4) $1.0 \times 10^{-14} \text{ cm}^2$
- 24. In Langmuir's model of adsorption of a gas on a solid surafce.
 - (1) The mass of gas striking a given area of surface is independent of the pressure of the gas.
 - (2) The adsorption at a single site on the surface may involve multiple molecules at the same time.
 - (3) The mass of gas striking a given area of surface is proportional to the pressure of the gas.
 - (4) The rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered.
- 25. From the following graphs, which two represent Langmuir Adsorption Isotherms?









26. If H₂ gas is made to absorb on a surface, then the fraction of surface area of adsorbent covered by gas molecules is proportional to:

 $(1) p^0$

- (2) p^2
- (3) $p^{1/2}$
- (4) p

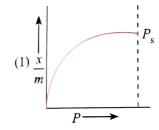
27. Which is correct in case of van der Waals' adsorption?

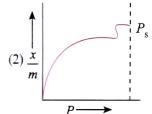
- (1) High temperature, high pressure
- (2) Low temperature, high pressure
- (3) Low temperature, low pressure
- (4) High temperature, low pressure

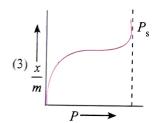
28. The most adsorbed gas on an activated charcoal is:

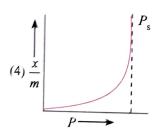
- (1) CH₄
- $(2) H_{2}$
- $(3) CO_{2}$
- $(4) N_2$

29. Which of the following adsorption isotherms represents the adsorption of a gas by a solid involving multilayers of formation? $(P_s = \text{saturation pressure})$







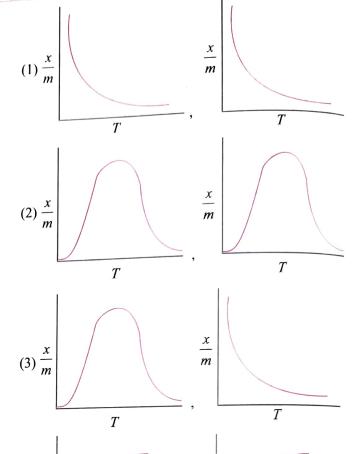


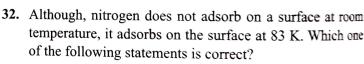
30. Which among the following statements is false?

- (1) Increase of pressure increases the amount of adsorption.
- (2) Increase of temperature may decrease the amount of adsorption.
- (3) Adsorption may be monolayered or multilayered.
- (4) Particle size of the adsorbent will not affect the amount of adsorption.

31. Select correct adsorption isobars for chemisorption and physisorption respectively:

(where
$$\frac{x}{m}$$
 = extent of adsorption, T = temperature)



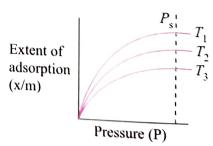


m

- (1) At 83 K, there is formation of monolayer.
- (2) At 83 K, nitrogen is adsorbed as atoms.

T

- (3) At 83 K, nitrogen molecules are held by chemical bonds.
- (4) At 83 K, there is formation of multimolecular layers.
- 33. For the graph below, select **correct** order of temperature?



 $(1) T_1 > T_2 > T_3$

 $(4) \frac{1}{m}$

- (2) $T_2 > T_3 > T_1$
- (3) $T_3 > T_2 > T_1$
- $(4) \ T_1 = T_2 = T_3$

Classification, Preparation and Properties of Colloidal Sol.

- 34. Zeta potential (or electrokinetic potential) is the
 - (1) Potential required to bring about coagulation of a colloidal sol.

- (2) Potential required to give the particles a speed of 1 cm s^{-1} in the sol.
- 3) Potential difference between fixed charged layer and the diffused layer having opposite charges.

(4) Potential energy of the colloidal particles.

- Blue colour of the sky is due to (1) Adsorption of light by dust particles
 - (2) Reflection of light by dust particles
 - (3) Scattering of light by dust particles
 - (4) Pressure of clouds which are a colloidal dispersion of water particles in air
- 16. Example of an intrinsic colloid is
 - (1) As₂S₃ sol
- (2) S sol
- (3) Egg albumin
- (4) Fe(OH)₃ sol
- If which of the following colloidal systems, fog is an
 - (1) Liquid dispersed in gas (2) Gas dispersed in gas
 - (3) Solid dispersed in gas (4) Solid dispersed in liquid
- 38. 1 mol of [Ag] Ag[⊕] sol is coagulated by
 - (1) 1 mol of KI
 - (2) 500 mL of 1 M K₂SO₄
 - (3) 300 mL of 1 M Na₃PO₄ solution
 - (4) 1 mol of AgI
- 39. Arsenic(III) sulphide forms a sol with a negative charge. Which of the following ionic substances should be most effective in coagulating the sol?
 - (1) KCl
- (2) MgCl₂
- $(3) Al_2(SO_4)_3 (4) Na_3PO_4$
- 40. Aluminium hydroxide forms a positively charged sol. Which of the following ionic substances should be most effective in coagulating the sol?
- (1) NaCl
- (2) CaCl₂
- (3) $Fe_2(SO_4)_3$ (4) K_3PO_4
- 41. Brownian motion is a/an
 - (1) Electrical property
- (2) Mechanical property
- (3) Optical property
- (4) Colligative property
- 42. The colligative property of a colloidal sol compared to the solution of non-electrolyte of same concentration will be
 - (1) Same
- (2) Higher
- (3) Lower
- (4) Higher or lower
- 43. Which of the following can act as a protective colloid?
 - (1) Gelatin
- (2) Silica gel
- (3) Oil-in-water emulsion (4) All correct
- 44. An emulsifier is an agent which (1) Accelerates the dispersion
 - (2) Homogenizes an emulsion
 - (3) Stabilizes an emulsion
 - (4) Aids the flocculation of an emulsion
- The stabilization of a dispersed phase in a lyophobic colloid is due to
 - (1) The adsorption of charged substances on dispersed phase.

- (2) The large electro-kinetic potential developed in the colloid.
- (3) The formation of an electrical layer between two phases.
- (4) The viscosity of the medium.
- 46. The diameter of colloidal particle is of the order
 - $(1) 10^{-3} \text{ m}$
- $(2) 10^{-6} \text{ m}$
- $(3) 10^{-15} \,\mathrm{m}$
- $(4) 10^{-7} \text{ m}$
- 47. The process of passing of a precipitate into colloidal solution on adding an electrolyte is called
 - (1) Dialysis
- (2) Peptization
- (3) Electrophoresis
- (4) Electro-osmosis
- 48. Tyndall effect is not observed in
 - (1) Suspension
- (2) True solution
- (3) Emulsions
- (4) Colloidal solution
- 49. The process of removing dissolved impurities from a colloidal system by means of diffusion through suitable membrane under the influence of an electric field is called
 - (1) Electro-osmosis
- (2) Electrodialysis
- (3) Electrophoresis
- (4) Peptization
- 50. The migration of positively charged colloidal particles, under an electrical field, towards the cathode is called
 - (1) Cataphoresis
- (2) Electro-osmosis
- (3) Sedimentation
- (4) Electrodialysis
- 51. Smoke is a dispersion of
 - (1) Gas in gas
- (2) Gas is solid
- (3) Solid in gas
- (4) Liquid in gas
- 52. The colloidal sol of As₂S₃ prefers to adsorb
 - (1) NO₃[⊙]
- (2) K[⊕]

 $(3) S^{2-}$

- (4) H[⊕]
- 53. A freshly formed ppt of SnO₂ is peptized by a small amount of NaOH. These colloidal particles may be represented as
 - (1) $[SnO_2]SnO_3^{2-}$; $2Na^{\oplus}$
- (2) $[SnO_2] Sn^{4+}; O^{2-}$
 - (3) $[SnO_2]Na^{\oplus}$; OH^{\odot}
- (4) $[SnO_2] Sn^{4+}$; OH[©]
- 54. Smoke has generally blue tinge. It is due to
 - (1) Scattering
- (2) Coagulation
- (3) Brownian motion
- (4) Electro-osmosis
- 55. Oil-soluble dye is mixed with water-in-oil emulsion, then
 - (1) Dispersion medium is coloured
 - (2) Dispersed phase is coloured
 - (3) Both coloured
 - (4) None is coloured
- 56. An oil-soluble dye is mixed with emulsion and the emulsion remains colourless. Then, it is
 - (1) O-in-W
 - (2) W-in-O
- (3) O-in-O
- (4) W-in-W
- 57. There is no scum formation when hard water is being used. The washing powder can be
 - (1) C₁₇H₃₅COONa
- -SO₃Na
- (3) Both
- (4) None

5.44	Physical Chemistry		(4) Both, the nature and	d magnitude of the charge of the
58.	Micelles are (1) Ideal solution (2) Associated colloids (4) Absorbent solutes		for As ₂ S ₃ colloid?	vill have highest coagulating power (2) Na [®]
	(3) Adsorbed surfaces (b) Formula (compared to common colloidal sols micelles have: (c) Higher colligative properties (d) Lower colligative properties (e) Same colligative properties (f) Formula (compared to common colloidal sols micelles have: (i) Higher colligative properties (ii) Same colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Higher colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Higher colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Higher colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Higher colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Higher colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Higher colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Higher colligative properties (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common colloidal sols micelles have: (iii) Formula (compared to common col	67.	(1) A1 ³⁺ (3) SO ₄ ^{2−} 1 mol of [AgI] Ag [⊕] can (1) 1 mol of AgNO ₃ (3) 2/3 mol of AgNO ₃	(4) PO ₄ ³⁻ be coagulated by: (2) 1/2 mol of AgNO ₃ (4) None of these

- 60. Which one of the following statements is correct? (1) Brownian movement is more pronounced for smaller particles than for bigger ones.
 - (2) Sols of metal sulphides are lyophilic.
 - (3) Hardy Schulze law states, the bigger the size of the ion, the greater is its coagulating power.
 - (4) One would expect charcoal to adsorb chlorine more strongly than hydrogen sulphide.
- 61. Gold number of a lyophilic sol is such a property that
 - (1) The larger its value, the greater is the peptizing power.
 - (2) The lower its value, the greater is the peptizing power.
 - (3) The lower its value, the greater is the protecting power.
 - (4) The larger its value, the greater is the protecting power.
- 62. Select the incorrect statement about micelles.
 - (1) They are associated.
 - (2) Surfactant molecules form micelles.
 - (3) They are formed above CMC and above the kraft temperature.
 - (4) Above CMC, the surfactant molecules undergo dissociation.
- 63. Select the incorrect statement:
 - (1) Micro emulsion and micellar solution are used to describe concentrated sufactant stabilized dispersion of water and hydrocarbons that are used to enhance petroleum recovery.
 - (2) Purple of cassius is Au sol. in water and is used to raise vitality in human system.
 - (3) Bredig's are method that cannot be used for the preparation of colloidal sol. of sodium.
 - (4) High charge density is the most important factor which gives rise to peculiar properties of colloids.
- **64.** Select the incorrect statement:
 - (1) Brownian motion is more effective for small particles than the bigger ones
 - (2) Brownian motion is due to impact of molecules of the dispersion medium on the colloidal particles.
 - (3) Black diamonds are dispersion of solid in solid.
 - (4) Blood contains negative as well as positively charged particles.
- **65.** Flocculating value of ion depends on:
 - (1) The shape of flocculating ion.
 - (2) The amount of flocculating ion.
 - (3) Nature of the charge on the flocculating ion.

- (3) 2/3 mol of AgNO₃
- (4) None of these
- 68. The coagulation of 100 mL of colloidal solution of gold $_{i_{S}}$ completely prevented by addition of 0.25 g of a substance "X" to it before addition of 1 mL of 10% NaCl solution The gold number of "X" is:
 - (1) 0.25

(2)25

(3)250

- (4) 2.5
- 69. Which of the following mixture will lead to the formation of negatively charged colloid [AgI]I[©]?
 - (1) 50 mL of 0.1 M AgNO₃ + 50 mL of 0.1 M KI
 - (2) 50 mL of 0.1 M AgNO $_3$ + 50 mL of 0.2 M KI
 - (3) 50 mL of 0.2 M $AgNO_3 + 50$ mL of 0.1 M KI
 - (4) 50 mL of 0.2 M AgNO $_3$ + 50 mL of 0.2 M KI
- 70. Arsenous sulphide sol is prepared by passing H₂S through arsenous oxide solution. the charge developed on the particles is due to adsorption of:
 - (1) H[⊕]

(3) OH

- $(4) O^{2-}$
- 71. Select incorrect statement:
 - (1) Gold sol is multimolecular coloid.
 - (2) Large number of particles of a substance aggregate together and formed multimolecular colloids.
 - (3) Metal sulphides are lyophobic colloids.
 - (4) Sulphur sol is multimolecular colloid and hydrophilic in nature.
- **72.** Select incorrect statement:
 - (1) Soap and detergent lower the interfacial surface tension between oil and water.
 - (2) Basic principle of peptization is reverse of coagulation.
 - (3) Soap and detergent are used as emulsifiers.
 - (4) Lyophilic sols need stabilizing agent.
- 73. For the coagulation of 50 mL of ferric hydroxide sol, 10 mL of 0.5 M KCl is required. What is the coagulation value of KCl?
 - (1)5

(2) 10

(3) 100

- (4) None of these
- 74. 100 mL of 0.6 M acetic acid is shaken with 2 g activated carbon. The final concentration of the solution after adsorption is 0.5 M. What is the amount of acetic acid adsorbed per gram of carbon?
 - (1) 0.6 g
- (2) 0.3 g
- (3) 1.2 g
- (4) None of these

Catalyst increases the rate by Catalysis

(1) Decreasing $E_{\rm a}$

(2) Increasing E_a

(3) Decreasing pressure

(4) Increasing entropy

(3) people which of the following catalyst is used during the hydrogenation of oil?

(1) Fe

(2) Ni

(4) Mo

(3) Pt which of the following is present at the time of cracking of hydrocarbons?

(1) Copper

(2) Zeolite

(3) Nickel

(4) Molybdenum

Which is not the correct statement for a catalyst?

(1) It does not alter E_a .

(2) The surface of a catalyst adsorbs reactants.

(3) Catalyst may form intermediates with reactants.

(4) Action of enzyme catalyst is always specific.

9. Match column A (catalyst) with column B (process)

A

1. SiO,

I. Cracking of Hydrocarbon

2. Pt 3. Zeolites II. of benzene

(1) $1 \rightarrow I$, $2 \rightarrow II$, $3 \rightarrow III$

III. Automobile converter (2) $1 \rightarrow III$, $2 \rightarrow II$, $3 \rightarrow 1$

(3) $1\rightarrow II$, $2\rightarrow III$, $3\rightarrow I$

(4) $1 \rightarrow III$, $2 \rightarrow I$, $3 \rightarrow II$

80. Catalyst used in polymerization of ethene is:

(1) TiCl₄ and AlR₃

(2) Fe, Co

(3) H₃PO₄

(4) Zeolites

- 81. Which is/are correct statements about the role of a catalyst in a reaction?
 - (1) It is reactant in a rate-determining step and then a product of some subsequent step.
 - (2) It provides an alternate mechanism with a lower energy of activation.
 - (3) It increases the rate of chemical reaction but does not itself undergo a permanent change during the course of the reaction.
 - (4) All of these.
- 82. Energy of activation of forward and backward reaction are equal in cases (numerical values) where
 - $(1) \Delta H = 0$
 - (2) No catalyst present
 - (3) $\Delta S = 0$
 - (4) Stoichiometry is the mechanism
- 83. Select the correct statement.
 - (1) Homogeneous catalysis occur at the interface of phases.
 - (2) Hydrolysis of protein in stomach and in intestine takes place due to the action of enzyme trypsin in stomach and pepsin in intestine
 - (3) ZsM 5 is used to convert toluene to benzene.
 - (4) Negative catalyst physically changes at the end of reaction.

84. In which of the following reactions heterogeneous catalysis is involved?

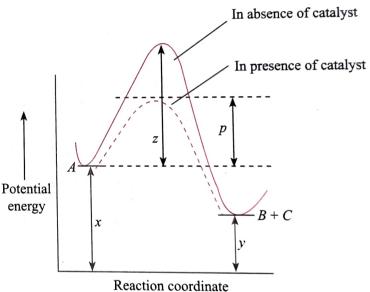
i.
$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

ii.
$$2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

iii.
$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

iv.
$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$$

- (1) (ii), (iii)
- (2) (ii), (iii) and (iv)
- (3) (i), (ii) and (iii)
- (4) (iv)
- 85. Air can oxidize sodium sulphite in aqueous solution but cannot do so in the case of sodium arsenite. If however, air is passed through a solution containing both sodium sulphite and sodium arsenite then both are oxidized. This is an example of:
 - (1) Positive catalysis
- (2) Negative catalysis
- (3) Induced catalysis
- (4) Auto-catalysis
- 86. For the reaction $A \rightarrow B + C$; the energy profile diagram is given in the figure:



What is the decrease in energy of activation in presence of catalyst?

(1)z

(2) z - p

(3) y - z

- (4) z x
- 87. The rate of a certain biochemical reaction catalysed by an enzyme in human body is 104 times faster than when it is carried out in the laboratory. The activation energy of this reaction:
 - (1) Is zero
 - (2) Is different in both the cases
 - (3) Is the same in both the cases
 - (4) None of the above
- 88. A catalytic poison renders the catalyst ineffective because:
 - (1) It is preferentially adsorbed on the catalyst.
 - (2) It adsorbs the molecules of the reactants.

5.46 Physical Chemistry

- (3) It combines chemically with the catalyst.
- (4) It combines chemically with one of the reactants.
- 89. An inhibitor is essentially:
 - (2) A negative catalyst
- (2) A heterogeneous catalyst
- (3) An auto catalyst
- (4) A homogeneous catalyst
- 90. Identify the correct statement regarding enzymes:
 - (1) Enzymes are specific biological catalysts that normally works at high temperature
 - (2) Enzymes are normally heterogeneous catalysts which decrease the reaction rate
 - (3) Enzymes are specific biological catalysts with low molar
 - (4) Enzymes are specific biological catalysts that are very specific in nature

Miscellaneous

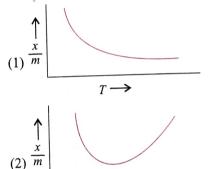
- 91. The gold numbers of protective colloids A, B, C, and D are 0.04, 0.002, 10, and 25, respectively. The protective powers of A, B, C, and D are in the order
 - (1) A > B > C > D
- (2) B > A > C > D
- (3) D > C > A > B
- (4) D > C > B > A
- 92. When 6×10^{-5} g of a protective colloid was added to 20 mL of a standard gold sol, the precipitation of latter was just prevented on addition of 2 mL of 10% NaCl solution. The gold number of a protective colloid is
 - (1) 3
- $(2) 3 \times 10^{-5}$ (3) 0.06
- (4) 0.03
- 93. In an experiment, addition of 4.0 mL of 0.005 M BaCl, to 16.0 mL of arsenious sulphide sol just causes the complete coagulation in 2 h. The flocculating value of the effective ion is:
 - (1) Cl° , 1.0 (2) Cl° , 2.0 (3) Ba^{2+} , 1.0 (4) Ba^{2+} , 0.5
- 94. A freshly obtained precipitate of SnO₂ is peptized by little of KOH to give a sol. The sol particles may be represented as
 - (1) $[SnO_2]K^{\oplus}$
- $(2) [SnO_2]OH^{\odot}$
- $(3) [SnO_2]Sn^{4+}$
- $(4) [SnO_2]SnO_3^{2-}$

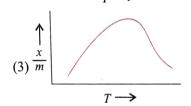
Multiple Correct Answers Type

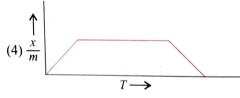
Adsorption

- 1. Which of the following increase(s) the activation of a solid adsorbent?
 - (1) Polishing the surface of the solid adsorbent.
 - (2) Subdividing the solid adsorbent.
 - (3) Blowing superheated steam through the porous adsorbent.
 - (4) Adsorption at very low pressure.
- 2. Which of the following statements is/are correct?
 - (1) Physical adsorption is multilayer, non-directional, and non-specific.
 - (2) In some cases, solvent may be adsorbed in preference to the solute on the surface of the adsorbent.

- (3) Chemical adsorption increases with increase in temperature.
- (4) Due to adsorption, surface energy increases.
- 3. Which one of the following is/are correct statement for physisorption?
 - (1) It is a reversible process.
 - (2) It requires less heat of adsorption.
 - (3) It requires activation energy.
 - (4) It takes place at low temperature.
- 4. Which of the following statements is/are correct?
 - (1) Increase of pressure increases the amount of adsorption.
 - (2) Increase of temperature may decrease the amount of adsorption.
 - (3) The adsorption may be monolayered or multilayered.
 - (4) Particle size of the adsorbent will not affect the amount of adsorption.
- 5. Which is not the adsorption isobar for chemisorption?

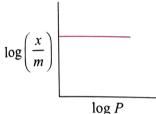






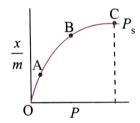
- 6. Which of the following is/are application(s) of adsorption?
 - (1) De-ionization of water
 - (2) Gas masks
 - (3) Hygroscopic nature of CaCl,
 - (4) Heterogeneous catalysis
- 7. Select the correct statement(s) among the following:
 - (1) At 83 K, N₂ is physisorped on the surface of iron.
 - (2) At 772 K and above N_2 is chemisorped on the iron surface.
 - (3) Activation energy is +ve in case of physisorption and zero in case of chemisorption.
 - (4) Activation energy is zero in case of physisorption and +ve in case of chemisorption.

- 8, Select the correct statement(s): Selection (1) Physical adsorption is reversible, has low heat of adsorption
 - (2) Physical adsorption forms unimolecular layer and takes place at low temperature and decreases with increase in temperature
 - (3) Physical adsorption is due to van der Waal's forces.
 - (4) Emulsifiers do not work on the principle of adsorption
- 9. Adsorption isotherm of $\log \left(\frac{x}{m}\right)$ and $\log P$ was found of



This is incorrect when:

- (1) P = 0
- (2) P = 1
- $(3) \frac{1}{-} = 1$
- (4) P < 1
- 10. In the given isotherm select the **correct** statement:



- (1) $\frac{x}{m} \propto P^{1/n}$ along OA
- (2) $\frac{x}{m} \propto P^0$ when point B is reached
- (3) $\frac{x}{m}$ does not increase rapidly with pressure along BC due to less surface area available for adsorption
- (4) Nature of isotherm is different for two gases for same adsorbent
- 11. If adsorption of a gas on a solid is limited to monolayer formation, then which of the following statement(s) is/are true?
 - (1) At low pressures, $\frac{x}{m}$ varies proportionately with p
 - (2) At moderate pressures, $\frac{x}{m}$ varies less than proportionately with p

 - (3) At hogh pressures, $\frac{x}{m}$ becomes independent of p(4) At high pressures, $\frac{x}{m}$ varies more than proportionately
- 12. Select the correct statement(s):
 - (1) Physisorption is favoured by low temperature
 - (2) Chemisorption is favoured by very high temperature because the process is endothermic

- (3) Chemisorption increases with increase in temperature owing to high activation energy
- (4) Oxygen adsorbed by charcoal can be desorbed by lowering pressure and temperature

Classification, Preparation and Properties of Colloidal Sol.

- 13. Which of the following is/are correctly matched?
 - (1) Butter-gel
- (2) Milk-emulsion
- (3) Fog–aerosol
- (4) Dust-solid sol
- 14. Which of the following is/are elastic gel?
 - (1) Gelatin
- (2) Silicic acid
- (3) Agar agar
- (4) Starch
- 15. Which of the following is/are negatively charged sol?
 - (1) Gold sol
- (2) Prussian blue dye
- (3) Haemoglobin
- (4) Starch
- 16. Which of the following is/are aerosols?
 - (1) Smoke
- (2) Milk
- (3) Butter
- (4) Fog
- 17. Which of the following is/are lyophobic colloids?
 - (1) Gold sol
- (2) As₂S₃ sol
- (3) Fe(OH)₃ sol
- (4) Starch sol
- 18. Which of the following is/are not correctly matched?
 - (1) Emulsion-curd
- (2) Foam-mist
- (3) Aerosol–smoke
- (4) Solid sol-cake
- 19. Which of the following electrolytes will not be most effective in the coagulation of gold sol?
 - (1) NaNO₃
- $(2) K_4[Fe(CN)_6]$
- (3) Na₃PO₄
- (4) MgCl₂
- 20. Which of the following are macromolecular colloids?
 - (1) Starch
- (2) Soap
- (3) Detergent
- (4) Cellulose
- 21. Isoelectric point is the pH at which colloidal particles
 - (1) Coagulate
 - (2) Become electrically neutral.
 - (3) Can move toward either electrodes
 - (4) None of these
- 22. Tyndall effect is applicable when
 - (1) The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
 - (2) The diameter of the dispersed particles is much smaller than the wavelength of the light used.
 - (3) The refractive indices of the dispersed phase and the dispersion medium must be same.
 - (4) The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude.
- 23. Multimolecular colloids are present in
 - (1) Sol of sulphur
- (2) Sol of protein
- (3) Sol of gold
- (4) Soap solution
- **24.** Select the correct statement(s).
 - (1) Aerosol is a colloidal solution of liquid in gas while gel is a colloidal solution of solid in liquid.
 - (2) Foam is a colloidal solution of gas in liquid while emulsion is a colloidal solution of liquid in liquid

- (3) Starch, gelatin and gum are lyophilic in nature
- (4) At CMC, the surfactant molecules undergo aggregation, micelle formation and reduction in surface tension of water.
- 25. Select the incorrect statement(s):
 - (1) Electrophoresis, Brownian movement and maxwell distribution are the properties of colloidal sols.
 - (2) Peptisation, electrophoresis at high potential and freezing can destroy the emulsion
 - (3) Mechanical disintegration method is used for the preperation of colloidal graphite and printing ink.
 - (4) Mechanical disintegration method is suitable when dispersion medium is an organic liquid
- 26. Which of the following statements is/are true?
 - (1) Flocculation value is inversely proportional to coagulating power
 - (2) Colloidal silica is protective colloid
 - (3) Alum is used for cleaning muddy water
 - (4) Gelatin is added in ice cream, it acts as an emulsifier.
- 27. Which of the following statements is/are correct?
 - (1) Mixing two oppositely charged sols neutralizes their charges and stabilizes the colloid
 - (2) Presence of equal and similar charges on colloidal particles provides stability to the colloids
 - (3) Any amount of dispersed liquid can be added to emulsion without destabilizing it
 - (4) Brownian movement stabilizes sols.

Catalysis

- 28. Which of the following statements is/are wrong?
 - (1) Zeolites are hydrated aluminosilicates which can be used as shape-selective catalysts.
 - (2) Enzymes show maximum activity when pH is either very low or very high.
 - (3) Enzymes show maximum activity at room temperature (20-25°C)
 - (4) Chemically, all enzymes are globular proteins.
- 29. Which of the following statements is/are not correct?
 - (1) A catalyst always increases the speed of a reaction.
 - (2) A catalyst does not take part in the reaction.
 - (3) A catalyst may affect the nature of the products formed.
 - (4) A catalyst is always an external substance added to the reaction mixture.
- 30. Which of the following belong(s) to the family of enzymes?
 - (1) Lipase
- (2) Pepsin
- (3) Ptylin
- (4) Cellulose
- 31. Which of the following is/are not possible in case of autocatalysis?
 - (1) Reactant catalysis
 - (2) Heat produced in the reaction catalysis
 - (3) Product catalysis
 - (4) Solvent catalysis

- 32. Which of the following is/are the characteristic of a catalyst?
 - (1) It changes equilibrium point.
 - (2) It alter the rate of reaction.
 - (3) It initiates the reaction.
 - (4) It increases the average KE of molecules
- 33. Which one of the followings is/are an example of homogeneous catalysis?
 - (1) Formation of SO₃ in the chamber process.
 - (2) Formation of SO₃ in the contact process.
 - (3) Hydrolysis of an ester in the presence of acid.
 - (4) Decomposition of KClO₃ in the presence of MnO₂.
- 34. Efficiency of the catalyst does not depend on its?
 - (1) Molecular weight
- (2) Number of free valencies
- (3) Physical state
- (4) Amount used
- 35. Which of the following statements is/are correct in the case of heterogeneous catalyst?
 - (1) The catalyst lowers the energy of activation.
 - (2) The catalyst actually forms a compound with the
 - (3) The surface of the catalyst plays a very important role.
 - (4) There is no change in the energy of activation.
- **36.** Select the correct statements:
 - (1) Heterogeneous catalyst lowers the energy of activation and reactant molecules are adsorbed on the surface of the catalyst
 - (2) Catalyst changes physically and quantitatively
 - (3) Ni is used in the hydrogenation of oil and thermite process does not involve any catalyst
 - (4) The decomposition of H_2O_2 , is slowed down by the addition of small amount of acetamide which acts as poison
- **37.** Which act(s) as negative catalyst?
 - (1) Lead tetraethyl as antiknock compound
 - (2) Glycerol in decomposition of H₂O₂
 - (3) Ethanol in oxidation of chloroform
 - (4) None of the above
- 38. Which of the following statement(s) is/are correct about solid catalyst?
 - (1) Same reactants may give different products by using different catalysts
 - (2) Catalyst does not change ΔH of reaction
 - (3) Catalyst is required in large quantities to catalyse reaction
 - (4) Catalytic activity of a solid catalyst does not depend upon the strength of chemisorption.

Linked Comprehension Type

Paragraph 1

A chemist studied the phenomenon of adsorption by putting blood charcoal in KCl solution. He observed difference in the behaviour with dilute KCl solution and with concentrated KCl solution. He studied the adsorption of different gases on solid adsorbent and adsorption. He are a business on solid adsorbent effect of temperature on adsorption. He put forward a model relationship relating x/m with equilibrian the energy that the energy that the put forward a multiplical relationship relating x/m with equilibrium pressure. Which of the following is correct?

- (1) Adsorption is always exothermic?
- (2) Adsorption is always endothermic.
- (3) Physical adsorption is endothermic whereas chemisorption is exothermic.
- (4) Chemical adsorption is endothermic whereas physical adsorption is exothermic.
- 2. Which of the following plot will be linear? (More than one
 - (1) Plot of $\log x/m$ versus P
 - (2) Plot of m/x versus 1/P
 - (3) Plot of log $\frac{P}{m/m}$ versus P
 - (4) Plot of $\log m/x$ versus $\log P$
- 3. The correct order of the adsorption of gases studied will be
 - $(1) NH_3 > SO_2 > CO_2 > HC1$
 - $(2) CO_2 > SO_2 > NH_3 > HC1$
 - $(3) SO_2 > NH_3 > HC1 > CO_2$
 - (4) $HC1 > SO_2 > NH_3 > CO_2$
- 4. Which of the following result is observed with the experiment of KCl solution?
 - (1) Dilute KCl solution shows no adsorption whereas concentrated KCl shows adsorption.
 - (2) Concentrated KCl solution shows positive adsorption whereas dilute KCl solution shows negative adsorption.
 - (3) Concentrated KCl solution shows no adsorption whereas dilute KCl solution shows adsorption.
 - (4) Dilute KCl solution shows positive adsorption whereas concentrated KCl solution shows negative adsorption.

Paragraph 2

Emulsions are also called the colloidal solutions in which the disperse phase as well as dispersion medium are liquids. It may be oil-in-water or water-in-oil type. Emulsifiers can be used to stabilize the emulsion. Soaps, detergents, proteins, and gums are used as emulsifiers.

- 5. Which of the following examples is/are oil-in-water-type emulsion?
 - (1) Ink
- (2) Detergent (3) Soap
- (4) Milk
- 6. Emulsion can be destroyed by (more than one correct)
- (1) The addition of emulsifier which tends to form another emulsion
 - (2) Electrophoresis with high potential
 - (3) Freezing
 - (4) All
- 7. Butter is an emulsion of type
 - (1) Water in oil
- (2) Oil in water
- (3) None
- (4) Both (1) and (2)

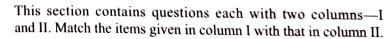
- 8. Addition of lyophilic solution to the emulsion forms
 - (1) A protective film around the dispersed phase
 - (2) A protective film around the dispersion medium.
 - (3) An aerosol
 - (4) True solution
- 9. Which of the following is homogeneous?
 - (1) Milk
- (2) Paint
- (3) Shampoo (4) All

Paragraph 3

There are certain substances which behave as normal, strong electrolyte at low concentration but at higher concentration they behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and the aggregated particles are called micelles. The formation of micelles takes place above certain concentration called critical micellization concentration (CMC) and a characteristic temperature.

- 10. Micelles are
 - (1) Emulsion-cum-gel
- (2) Adsorbed catalyst
- (3) Associated colloids
- (4) Ideal solutions
- 11. Micelles are formed only
 - (1) Above CMC and above the Kraft temperature
 - (2) Below CMC and the Kraft temperature
 - (3) Above CMC and below the Kraft temperature
 - (4) Below CMC and above the Kraft temperature
- 12. Above CMC, the surfactant molecules undergo (more than one correct)
 - (1) Aggregation
- (2) Micelles formation
- (3) Dissociation
- (4) All
- 13. What type of molecules form micelles?
 - (1) Non-polar molecules
 - (2) Polar molecules
 - (3) Surfactant molecules
 - (4) Salt of weak acid and weak base
- 14. Micelles are used in
 - (1) Detergents
- (2) Petroleum recovery
- (3) Magnetic separation
- (4) All of these

Matrix Match Type



1.		Column I		Column II
	a.	Dispersion of Al(OH) ₃ by small quantity of AlCl ₃	p.	Macromolecular colloid
	b.	Addition of large quantity of AlCl ₃ in (a)	q.	Selective adsorption
	c.	Solution of haemoglobin in water	r.	Flocculation
	d.	Chromatographic seperation of components of a solution	s.	Peptization

	F-8		Column II
	Column I		Solvent heating
a.	Gold number	p.	
-	Lyophobic	q.	Coagulation
b.		r.	Protective colloids
c.	Butter	-	Solvent
d.	Hardy Schulze rule	S.	
e.	Micelles	t.	Associated colloids
С.	Mileonet	u.	An emulsion

3.		Column I		Column II
		Purple of cassius	p.	Gel
	a. b.	Cheese	q.	Gold sol
	-	Dialysis	r.	Robert Brown
	c.	Brownian movement	s.	Hydrophilic
	e.	Water-loving colloids	t.	Purification of colloidal
		and the second		solutions

	Column I		Column II
a.	Liquid dispersed in gas	p.	Emulsifying agent
b.			Aerosol
ċ.	Hydrophobic	r.	Ultramicroscope
100		s.	Irreversible
e.	Electrophoresis	t.	Sewage disposal
f.	Soap	u.	Smoke precipitator

5.		Column I		Column II
	a.	Activated charcoal	p.	A device to adsorb poisonous gases
	b.	$x/m = KP^{1/n}$	q.	One of the adsorbents
Ì	c.	For humidity control	r.	Silica gel
	d.	Gas masks	s.	Freundlich adsorption isotherm

	Column I		Column II
a.	Physisorption	p.	Multimolecular
b.	Chemisorption	q.	High heat of activation
c.	Activated adsorption	r.	High temperature required
d.	Desorption	s.	Low pressure required
e.	Electro-osmosis	t.	Determination of charge on colloidal particles

	Column I		Column II
a.	Placing silica gel in water vapour	p.	Enzymatic catalysis
b.	Placing anhydrous CaCl ₂ in water vapour	q.	Occlusion

		r.	Adsorption
c.	Placing finely divided nickel in a closed vessel containing H ₂ gas		
	containing 12 8	s.	Absorption
d.	solution with blood		
	charcoal	-	Negative adsorption
e.	Conversion of proteins	t.	140guerro ausorption
	into amino acids		

erical		

1.	From the given following sol how many can coagulate the
	adobin sol?
	Fe(OH) ₃ , Ca(OH) ₂ , Al(OH) ₃ , starch, clay, As ₂ S ₃ , CdS, basic
	dye.

(1) 1 (2) 3

(3) 4

(4) 8

2. From the given following sol how many can coagulate silica acid sol?

Fe(OH)₃, Ca(OH)₂, Al(OH)₃, Starch, Clay, As₂S₃, CdS, Basic dye.

(1)4

(2) 3

(3)2

(4) 8

3. For the coagulation of 500 mL of arsenious sulphide sol, 2 mL of 1M NaCl is required. What is the flocculation value of NaCl?

(1) 3

(2) 2

(3)5

(4) 4

4. The coagulation of 100 mL of a colloidal sol of gold is completely prevented by addition of 0.03 g of haemoglobin to it before adding 1 mL of 10% NaCl solution. Calculate the gold number of haemoglobin.

(1)4

(2) 8

(3) 3

(4)9

5. The gold number of gelatin is 0.01. Calculate the amount of gelatin to be added to 1000 mL of a colloidal sol of gold to prevent its coagulation, before adding 1 mL of 10% NaCl solution.

(1) 2

(2) 1

(3)4

(4)5

6. 526.3 mL of 0.5 m HCl is shaken with 0.5 g of activated charcoal and filtered. The concentration of the filtrate is reduced to 0.4 m. The amount of adsorption (x/m) is

(1) 3

(2)6

(3) 8

(4) 4

7. In an experiment, addition of 5.0 mL, of 0.006 M BaCl₂ to 10.0 mL of arsenic sulphite sol just causes the complete coagulation in 34 h. The flocculating value of the effective ion is:

(1) 2

(2) 3

(3)4

(4)5

8. In an adsorption experiment, a graph between $\log (x/m)$ versus $\log P$ was found to be linear with a slope of 45°. The intercept on the y axis was found to be 0.301. Calculate the amount of the gas adsorbed per gram of charcoal under a pressure of 3.0 atm.

(1)4

(2) 2

(3)6

(4) 8

VICUINES

Correct Answer Type Which of the following statements is incorrect regarding which of the following statements is incorrect regarding physisorptions?

physiocer because of van der Waals forces.

(1) More easily liquefiable gases are adsorbed readily.

(2) More high pressure, it results into multimolecular layer adsorbent surface. on adsorbent surface.

Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is slow and positive. (AIEEE 2009)

cold numbers of protective colloids A, B, C, and D are 0.50, fold numbers of the correct order of their protective powers is

$$\int_{(1)}^{posecut \cdot a} ds < C < B$$

(2)
$$C < B < D < A$$

$$\int_{(3)A} A < C < B < D$$

(4)
$$B < D < A < C$$

(AIEEE 2009)

According to Freundlich adsorption isotherm which of the following is correct?

(1)
$$\frac{x}{m} \propto p^0$$

(2)
$$\frac{x}{m} \propto p^1$$

$$(3) \frac{x}{m} \propto p^{1/m}$$

(4) All of the above are correct for different range of pressure (AIEEE 2012)

1. The coagulating power of electrolytes having ions Na+, Al3+, and Ba^{2+} for arsenic sulphide solution increases in the order (1) $Al^{3+} < Ba^{2+} < Na^+$ (2) $Na^+ < Ba^{2+} < Al^{3+}$

(1)
$$Al^{3+} < Ba^{2+} < Na^{+}$$

(2)
$$Na^+ < Ba^{2+} < Al^{3+}$$

(3)
$$Ba^{2+} < Na^+ < Al^{3+}$$

(4)
$$Al^{3+} < Na^+ < Ba^{2+}$$

(**JEE Main 2013**)

² ³g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be $0.042\ N.$ The amount of acetic acid adsorbed (per gram of charcoal) is

- $^{(1)}18\,\mathrm{mg}$
- (2) 36 mg
- (3)42 mg
- (4) 54 mg

(**JEE Main 2015**)

For a linear plot of $\log (x/m)$ versus $\log p$ in a Freundlich Sotherm, which of the following statements is correct? (k and n are constants) $(1)\log(1/n)$ appears as the intercept

(2) $B_{0th} k$ and 1/n appear in the slope term (3) 1/n appears as the intercept

 $^{(4)}O_{n}$ $^{1/n}$ appears as the slope

The Tyndall effect is observed only when following conditions are satisfied.

(i) The diameter of the dispersed particles is much smaller than the wavelength of the light used.

(ii) The diameter of the dispersed particle is not much smaller than the wavelength of the light used.

(iii) The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude.

(iv) The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.

- (1)(i) and (iv)
- (2) (ii) and (iv)
- (3) (i) and (iii)
- (4) (ii) and (iii)

(JEE Main 2017)

JEE ADVANCED

Single Correct Answer Type

- 1. Among the following electrolytes, which is the most effective coagulating agent for Sb₂S₃ solution?
 - (1) Na₂SO₄
- (2) CaCl₂
- $(3) Al_2(SO_4)_3$
- (4) NH₄C1

(IIT-JEE 2009)

2. The coagulating power of electrolytes having ions Na^{\oplus} , Al^{3+} and Ba2+ for arsenic sulphide sol increases in the order:

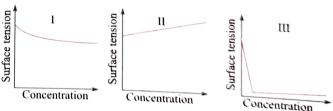
- (1) $Na^{\oplus} < Ba^{2+} < Al^{3+}$
- (2) $Ba^{2+} < Na^{\oplus} < Al^{3+}$
- (3) $Al^{3+} < Na^{\oplus} < Ba^{2+}$
- (4) $A1^{3+} < Ba^{2+} < Na^{\oplus}$

(JEE Advanced 2013)

- 3. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is
 - (1) The adsorption requires activation at 25°C
 - (2) The adsorption is accomanied by a decrease in enthalpy
 - (3) The adsorption increases with increase of temperature.
 - (4) The adsorption is irreversible

(JEE Advanced 2013)

4. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solution of KCl, CH3OH and CH₃(CH₂)₁₁OSO₃ Na⁺ at room temperature. The correct assignment of the sketches is



(1) I : KCl II : CH_3OH III : $CH_3(CH_2)_{11}$ $OSO_3^-Na^+$

(2) $1: CH_3(CH_2)_{11} OSO_3^- Na^+ II: CH_3OH III: KCI$

(3) I : KCl II : $CH_3(CH_2)_{11}OSO_3^- Na^+ III : CH_3OH$

(4) I: CH_3OH II: KCl III: $CH_3(CH_2)_{11}$ $OSO_3^ Na^+$ (JEE Advanced 2016)

Multiple Correct Answers Type

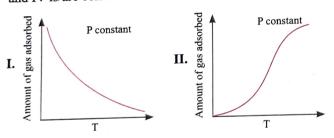
- 1. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is(are)
 - (1) Adsorption is always exothermic.
 - (2) Physisorption may transform into chemisorption at high temperature.
 - (3) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.
 - (4) Chemisorption is more exothermic than physisorption; however, it is very slow due to higher energy of (IIT-JEE 2011) activation.
- 2. Choose the correct reason(s) for the stability of the lyophobic colloidal particles.
 - (1) Preferential adsorption of ions on their surface from the solution.
 - (2) Preferential adsorption of solvent on their surface from the solution.
 - (3) Attraction between different particles having opposite charges on their surface.
 - (4) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

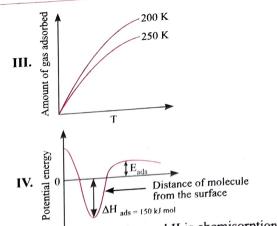
(IIT-JEE 2012)

55. (1)

60. (1)

3. The given graph/data I, II, III and IV represent general trends $\,$ observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is/are correct?





- (1) I is physisorption and II is chemisorption.
- (2) IV is chemisorption and II is chemisorption.
- (3) I is physisorption and III is chemisorption.
- (4) IV is chemisorption and III is chemisorption.

(IIT-JEE 2012)

16.

31

- 4. The correct statement(s) about surface properties is(are)
 - (1) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system
 - (2) The critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature
 - (3) Cloud is an emulsion type of coloid in which liquid is dispersed phase and gas is dispersion medium
 - (4) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution

(JEE Advanced 2017)

Answers Key

EXERCISES

51. (3)

56. (1)

Single Correct Answer Type

52. (3)

57. (2)

51,16.0				
1. (1)	2. (2)	3. (1)	4. (4)	5. (1)
6. (3)	7. (1)	8. (1)	9. (2)	10. (3)
11. (1)	12. (1)	13. (1)	14. (3)	15. (1,2)
16. (3,4)	17. (3)	18. (2)	19. (4)	20. (1)
21. (1)	22. (4)	23. (4)	24. (3)	25. (2)
26. (3)	27. (2)	28. (3)	29. (1)	30. (4)
` ,	32. (4)	33. (1)	34. (3)	35. (3)
31. (3)	37. (1)	38. (1,2)	39. (3)	40. (4)
36. (3)	42. (3)	43. (1)	44. (2)	45. (3)
41. (2)	. ,	48. (2)	49. (2)	50. (1)
46. (4)	47. (2)	70. (2)	•>• (~)	

53. (1)

58. (2)

54. (1)

59. (2)

65. (4) **62.** (4) 63. (4) 64.(4)**61.** (3) 70.(2) **69.** (2) 67.(4)**68.** (2) **66.** (1) **75.** (1,3) 74. (2) 73. (3) 71.(4) 72.(4) 80.(2) 77.(2) **78.** (1) **79.** (3) **76.** (2) **85.** (3) **84.** (1) 81. (4) **82.**(1) 83. (4) 90. (4) **89.** (1) 86. (2) 87.(2) 88. (1) 94. (4) 91.(2) 92. (4) **93**. (3)

Multiple Correct Answers Type

Multiple Correct	Answers Type	
1. (2, 3)	2. (1, 2)	3. (1, 2, 4)
4. (1, 2, 3)	5. (1, 2, 4)	6. (1, 2, 4)
7. (1, 2, 4)	8. (1, 3)	9. (1, 2, 4)
10. (1, 3, 4)	11. (1, 2, 3)	12. (1, 3, 4)
13. (1, 2, 3)	14. (1, 3, 4)	15. (1, 4)

	17. (1, 2, 3)	18. (1, 2, 4)
16.(1,4)	20. (1, 4)	21. (1, 2, 3)
10 (1, 2, 3)	23. (1, 3)	24. (1, 3, 4)
(1, 4)	26 (1 2 4)	27. (2, 4)
$\begin{array}{c c} 25.(1,2,4) \\ 25.(1,2,3) \end{array}$	29. (1, 2, 4)	30. (1, 2, 3)
18.(1, 2, 3)	32. (2, 3, 4)	33. (1, 3, 4)
31.(1, 2, 4)	35. (1, 2, 3)	36. (1, 3)
$\frac{31.(1,3,4)}{31.(1,2,3)}$	38. (1, 2)	
37. (1, 2, 3)	Lancian Type	

17.(1, 2, 3) linked Comprehension Type

1. (1)	2. (1,2,3)	3. (3)	4. (2)	5. (4
(2.3)	7. (1)	8. (1)	9. (1)	10. (1
g. (2)	12. (1,2)	13. (3)	14. (1)	`

Matrix Match Type

a	b	c	d	e	f
S	r	p	<u> </u>		_
r	S	u	q	t	
q	p	t	r	S	
q	r	S	t	u	р.
q	S	r	p	_	
p	q, r	q, r	S	t	
r	S	q	t	D .	_
	s r q q q	s r r s q p q r q s p q, r	s r p r s u q p t q r s q s r p q, r q, r	s r p r s u q q p t r q r s t q s r p p q, r q, r s	s r p — r s u q t q p t r s q r s t u q s r p — p q, r q, r s t

Numerical Value Type

1. (3)	2. (1)	3. (4)	4. (3)	5. (2)
6. (4)	7. (1)	8. (3)		

ARCHIVES

JEE Main

Single Correct Answer Type

1. (4)	2. (3)	3. (4)	4. (2)	5. (1)
6. (4)	7. (2)			

JEE Advanced

Single Correct Answer Type

1. (3)	2. (1)	3. (2)	4. (4)
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Multiple Correct Answers Type

	7,6-	
1. (1, 2, 4)	2. (1, 4)	3. (1, 3)
4. (2, 4)		() ,

Nuclear Chemistry

OVERVIEW

- 1. Nuclear chemistry deals with the phenomenon involving the nuclei of the atoms.
 - The phenomenon of spontaneous emission of certain kinds of radiations by same elements is called *radioactivity* and the *radioactive elements*.
- 2. The phenomenon of natural radioactivity was discovered by Henry Becquerel in 1896.
- Polonium and radium were isolated from pitchblende.
 Radium is about 2 million times more radioactive than uranium.
- 4. α -particles are helium nuclei (charge = +2 and mass = 4 amu). β -particles are electrons (charge = -1 and mass = very small).
- 5. α -rays are deflected towards negative plate of the electric field through a small angle where as β -rays are deflected towards positive plate through a larger angle and γ -rays do not undergo a large deflection.
- 6. Increasing penetrating power = $\alpha < \beta < \gamma$ Increasing ionizing power = $\gamma < \beta < \alpha$

Increasing luminosity on ZnS screen = $\gamma < \beta < \alpha$

- 7. Isotopes: Atoms of same element having same element having different mass numbers, e.g., $_1H^1$, $_1D^2$, $_1T^3$.
- 8. Isobars: Atoms of different elements having same mass numbers, e.g., C^{14} , N^{14} .
- 9. Isotones: Atoms of different elements having same number of neutrons
- 10. Isoelectronic: Atoms of different elements having same number of electrons.
- II. Isodiaphers: Elements which have the same value of (n-p) are called isodiaphers.
- 12. Isosters: Compounds having same number of atoms and same number of electrons, e.g., CO₂, N₂O etc.
- 13. Nuclides and their decay product after one α and two β particles are called isotopes.

$$A^{AZ} \xrightarrow{-\alpha} A_{-2}B^{Z-4} \xrightarrow{-\beta} A_{-2+1}C^{Z-4} \xrightarrow{-\beta}$$

$$A^{-2+1+1}D^{Z-4} \text{ or } A^{DZ-4}$$

Therefore, A and D are isotopes.

14. Nuclides and their decay product after β emission are called isobars.

 $_{1}H^{3} \xrightarrow{-\beta} _{2}He^{3}$

15. Nuclides and their decay product after α emission are called isodiaphers.

 $_{A}A^{Z} \xrightarrow{-\alpha} _{Z-2}B^{Z-4}$

- **16.** Nuclides which have an odd number of proton and odd number of neutrons are unstable (i.e., radioactive) and which do not have *N/P* ratio in the stability zone.
- 17. If the atomic number is below 82, then when N/P ratio is very low, it increases either by $\beta^{\oplus}({}_{+1}e^0)$ emission or K-capture $({}_{-1}e^0)$. The new N/P ratio of daughter element is $\left(\frac{N+1}{Z-1}\right)$. Here p changes to n and β^{\oplus} .

 $_{1}H^{1} \longrightarrow {_{0}}n^{1} + {_{+1}}e^{0}$.

- 18. If the atomic number is below 82, then when N/P ratio is very high, it decreases by $\beta^{\ominus}(_{-1}e^0)$ emission. The N/P ratio of the daughter element becomes $\left(\frac{N-1}{Z+1}\right)$. Here n changes to p and β^{\ominus} .
- 19. The changing of N/P ratio towards the stability of elements having atomic weight less than 82 is due to strong n-p and p-p attractive forces operating at nuclear distance.
- 20. If the atomic number is greater than 82, then the N/P ratio becomes stable by α -emission ($_2$ He⁴) leading to daughter element N/P ratio to $\left(\frac{N-2}{Z-2}\right)$.
- 21. For heavier nucleus, (p-p) repulsion forces start to offset the attractive forces. Therefore, the reduction of Z leads to the reduction of p-p repulsion, and excess of neutrons over protons are required for stability.
- 22. Up to $Z = 20 \longrightarrow$ Stability value of N/P = 1Up to $Z = 30 \longrightarrow$ Stability value of N/P = 1.13Up to $Z = 40 \longrightarrow$ Stability value of N/P = 1.25Up to $Z = 50 \longrightarrow$ Stability value of N/P = 1.40
 - Up to $Z = 60 \longrightarrow \text{Stability value of } N/P = 1.80$
 - Up to $Z = 80 \longrightarrow$ Stability value of N/P = 1.53

23. Nuclear radius is about 10^{-5} the radius of atoms. The density of the nucleus is very high $(10^{14} \text{ g cm}^{-3})$.

Radius (r) of the nucleus of any atom = $r = R_0 A^{1/3}$.

$$A = \text{mass number}, R_0 \text{ (constant)} = 1.3 \times 10^{-15} \text{ m}$$

= 1.3 × 10⁻¹³ cm

24. Unit for expressing the area of nuclear cross-section is barn $(1 \text{ barn} = 10^{-24} \text{ cm}^2 = 10^{-28} \text{ m}^2)$.

1 amu = 1.66×10^{-27} kg; 1 amu = 931.5 MeV

25. Radium of nucleus, $r = R_0 A^{1/3}$, where

 $R_0 = 1.4 \times 10^{-15}$, A = mass number

- 26. Group displacement law: It was proposed by Fajan, Soddy, and Russel in 1913. It states that when an α-particle is emitted, the daughter element has atomic number 2 units less than that of the parent element. It is consequently displaced two places (group) to the left in the periodic table. When a β-particle is emitted, the daughter element has an atomic number 1 unit higher than that of the parent element. It is consequently displaced one place (group) to the right in the periodic table. However, in the case of elements of lanthanide series (57–71) and actinide series (89–103), which belong to group 3, this law does not hold true.
 - **a.** In lanthanide series from element Pr to Tm, after α or β -emission, group 3 elements remain same for parent and daughter element.
 - **b.** Similarly, for actinide series, from element Pa to Md, after the emission of α or β -emission, group 3 elements remain same for parent and daughter element.

e.g.
$${}_{92}U^{238} - {}_{2}He^4 \longrightarrow {}_{90}Th^{234}$$

Group 3 Group 3

- 27. Binding energy is the energy released during the hypothetical formation of the nucleus from individual nucleus. It arises from the fact that the mass of a nucleus is less than the mass of the sum of the nucleons. The difference is called *mass defect*. Binding energy is a measure of the stability of the nucleus. Nuclei with mass number around 60 have higher binding energy and hence more stable.
- 28. Packing fraction = $\frac{\text{Isotopic mass Mass number}}{\text{Mass number}} \times 10^4$
- 29. Kinetic equation of radioactive decay:

 $N = N_0 e^{-Kt}$ (exponential form)

30.
$$K = \frac{2.303}{t} \log \frac{N_0}{N} = \frac{2.303}{t} = \log \frac{a}{a - x}$$

where K is the disintegration constant or decay constant (in time⁻¹), N_0 is the number of atoms of the radioactive substance originally present, N is the number of atoms present at any time t, a is the amount initially present, and a-x is the amount present at time t.

- **31.** Half-life period, $t_{1/2} = 0.693/K$.
- 32. Average life period, $\lambda = 1/K = t_{1/2}/0.693 = 1.44t_{1/2}$. In nuclear chemistry chapter, quite often symbol λ is used in place of K.

33. In a disintegration series, for intermediate consecutive atoms A, B, C, etc., in equilibrium,

$$K_{\mathbf{A}}N_{\mathbf{A}} = K_{\mathbf{B}}N_{\mathbf{B}} = K_{\mathbf{C}}N_{\mathbf{C}}.$$

or
$$\frac{N_{\rm A}}{N_{\rm B}} = \frac{K_{\rm B}}{K_{\rm A}} = \frac{(t_{1/2})_{\rm A}}{(t_{1/2})_{\rm B}}$$

34. Amount (N) of the substance left after n half lives

$$= N = N_0 \left(\frac{1}{2}\right)^n$$
, where N_0 is the amount or number of $atom_S$

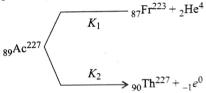
initially present and n is the number of half lives.

$$n = \frac{\text{Total time}}{t_{\text{trans}}}$$

- **a.** A radioactive element undergoes 50% decay in one half life.
- **b.** The time in which 63.2% radioactive element undergoes decay is called average life λ .
- c. The radioactive element undergoes 99.9% decay in 10 times of half life.

or
$$t_{99.9\%} = 10t_{1/2}$$

- **d.** An element undergoes 75% is two times of half life. or $t_{75\%} = 2t_{1/2}$
- **e.** $t_{25\%} = 0.4t_{1/2}$
- f. Total life span of a radioactive element is infinite.
- 35. Some radioactive elements undergo α and β -decay in parallel path.



Overall decay constant $K = K_1 + K_2$

Fractional yield of Fr =
$$\frac{K_1}{K}$$

Fractional yield of Th = $\frac{K_2}{K}$

36. At equilibrium,

$$A \longrightarrow B \longrightarrow C \dots$$

$$\frac{\text{Amount of A}}{\text{Amount of A}} = \frac{K_A}{K_B} = \frac{(t_{1/2})_B}{(t_{1/2})_A}$$

37. Unit of rate of decay:

1 curie (Ci) =
$$3.7 \times 10^{10}$$
 dis s⁻¹

1 millicurie (mCi) =
$$3.7 \times 10^7$$
 dis s⁻¹

1 microcurie (
$$\mu$$
Ci) = 3.7 × 10⁴ dis s⁻¹

1 rutherford (Rd) =
$$10^6$$
 dis s⁻¹

1 millicurie (mCi) = 37 rutherford

1 becquerel (Bq) = 1 dis s^{-1}

Radius (r) of the nucleus of any atom = $r = R_0 A^{1/3}$

38.
$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log \frac{a}{(a-x)}}$$

$$\begin{cases} x\% = \text{Percentage of radioactive} \\ \text{substance decomposed} \\ a = \text{Initial amount of substance} \\ a - x = \text{Amount of substance left} \end{cases}$$

$$\frac{\log\left(\frac{a}{a-x}\right)}{\int_{y\%}^{y} = \log\frac{a}{(a-y)}}$$

$$\frac{\log\left(\frac{a}{a-x}\right)}{\log\frac{a}{(a-y)}} \qquad \begin{bmatrix} a-x = \text{Amount of substance} \\ x \text{ left} \\ a-y = \text{Amount of substance} \\ y \text{ left} \end{bmatrix}$$

Rate $\left(\frac{-\partial N}{\partial t}\right)$ of radioactive decay is given as:

$$\frac{-\partial N}{\partial t} = K \times \frac{\text{Mass}}{\text{Atomic mass}} \times 6.023 \times 10^{23}$$
$$= \frac{0.693}{t_{1/2}} \times \frac{\text{Mass}}{\text{Atomic mass}} \times 6.023 \times 10^{23}$$

11. The various disintegration series are:

Series		Starting element	Stable end product	Value of n for the starting element	the
4n	Thorium series	Th-232	Pb-208	58	52
4n + 1	Neptunium series*	Pu-241	Bi-209	59	52
4n + 2	Uranium series	U-238	Pb-206	59	51
4n+3	Actinium series	U-235	Pb-207	58	51

*It is an artificial series.

- 42. Magic numbers: The extra stable nuclei having large number of isotopes have fully filled nuclear shells (i.e., have closed shells). These are the shells which contain 2, 8, 20, 50, 82, or 126 neutrons or protons. These numbers are therefore called magic number of the nuclear shells.
- 43. Out of protons, neutrons, α -particles, β -particles, etc., neutrons are the best bombarding particles because they are neutral and have significant mass.
- 44. Cyclotron, synchotron, and bevatron are the machines used for accelerating the particles.
- 45. Artificial/induced radioactivity means making a stable nucleus radioactive on bombardment with a suitable particle. It was discovered by Irene Curie and her husband F. Joliot in 1934.

e.g.,
$${}_{2}\text{He}^{4} + {}_{13}\text{Al}^{27} \longrightarrow {}_{15}\text{P}^{30} + {}_{0}n^{1}$$

$${}_{15}\text{P}^{30} \longrightarrow {}_{14}\text{Si}^{30} + {}_{1}e^{0}$$

- 46. Artificial radioactivity can be induced in elements with low atomic numbers but natural radioactivity is shown by elements with high atomic number (>83).
- 47. Nuclear fission: Process in which a heavy nucleus breaks up into two smaller nuclei on bombardment with nucleus. $_{92}\mathrm{U}^{235} + _{0}n^{1} \rightarrow _{92}\mathrm{U}^{236} \longrightarrow _{56}\mathrm{Ba}^{140} + _{36}\mathrm{Kr}^{93} + 3_{0}n^{1}$
- 48. Critical mass: Minimum mass of fissionable material required that leads to a self-sustaining chain fission reaction for $_{92}\mathrm{U}^{235}.$ The critical mass is between 1 and 100 kg.
- 49. Nuclear fusion: The process in which two nuclei of light atom fuse to form heavy nuclei with the liberation of large amount of energy.

$$_{1}H^{2} + _{1}H^{2} \rightarrow _{2}He^{4} + 23 \times 10^{8} \text{ kJ mol}^{-1}$$

- 50. Fusion reactions are thermonuclear reactions which require very high temperature ($>10^6$ K).
- 51. The only nuclei which undergo nuclear fission are U-235 and Pu-239.
- 52. The control rods used in a nuclear reactor are made up of Cd-113 or B-10. They can absorb neutrons.
- 53. Heavy water (D₂O) is used as a moderator in the nuclear reactor. It slows down the speed of neutrons. It also acts as a coolant.
- 54. Elements with atomic numbers greater than 92, i.e., which come after uranium, are called transuranic elements. Except plutonium which has a half life of about 24,000 years, all other have very short, half, lives.
- 55. The actinide series is complete at element with Z = 103(lawrencium). Elements with Z = 104-109 are d-block elements. These are called transactinides or super heavy elements. Thus, transuranic elements include transactinide. Most of these elements have been synthesized by artificial transmutation. Hence, they are called synthetic elements.
- 56. The difficulty in the synthesis of transactinides lies in the fact that they have been obtained by bombardment with medium weight nuclei and it is extremely expensive to build accelerators which can accelerate them.
- 57. The radioisotope generally used in the treatment of cancer is Co-60. I-131 is used in the treatment of thyroid disorders and P-32 in the treatment of leukemia.
- 58. The age of minerals and rocks is calculated from the amount of lead present a long with a definite amount of uranium (U-PB method) or He along with U, called helium dating.
- **59.** Radiocarbon dating is used for predicting the age of fallen tree or dead animal form the knowledge of the ratio of C-14/C-12 present in the sample as compared to that in the atmosphere or fresh wood.

6.1 INTRODUCTION

Nuclear chemistry is concerned with nuclear stability and the process of nuclear changes. Thus, the branch of chemistry dealing with the phenomenon involving the nuclei of the atoms is known as nuclear chemistry.

The phenomenon of spontaneous emission of highly penetrating radiations by heavier elements of the periodic table is called *natural radioactivity* and the elements showing this property are called *radioactive elements*. Radioactivity is essentially a nuclear phenomenon. The experimental evidence reveals that the phenomenon of radioactivity is not at all affected by the imposed conditions of temperature, pressure, chemical combinations, etc. Therefore, electrons orbiting the nucleus were not responsible for radioactivity. Hence, radioactivity must be the property of heavy nuclei only. In the universe, there are only 81 stable elements having one or more non-radioactive isotopes. No stable isotope exists for the elements above 83 Bi²⁰⁹. Thus, bismuth is the heaviest stable nuclide. Two earlier elements technetium and promethium exist only as radioactive isotope.

6.2 DISCOVERY OF RADIOACTIVITY

The phenomenon of radioactivity was accidentally discovered by French scientist Henri Becquerel who in 1896 reported that uranium salts emitted a radiation with properties similar to X-rays (discovered earlier by Rontgen, 1895).

After the discovery of radioactivity, Marie Curie and Pierre in later years led to the discovery that the atoms of certain other elements such as thorium, radium, and polonium undergo spontaneous decay and emit similar radiations. Since that time more than 40 elements have been found to exhibit natural radioactivity, and a large number of elements have been made radioactive by artificial means.

6.3 NATURE OF RADIOACTIVE RADIATIONS

The nature of the radiations emitted from a radioactive substance was investigated by Rutherford and his co-workers in 1904 by applying electric and magnetic field to the radiations as shown in Fig. 6.1. It is observed that on applying the field, the rays emitted from the radioactive substance are split into three types. The rays which are attracted towards the negative plate are positively charged and are called alpha (α) rays. The rays which are deflected towards the positive plate are negatively charged and are called beta (β) rays. The third type of rays which are not deflected on any side but move straight are known as gamma (γ) rays. Further, β -rays are deflected to a much greater extent than α -rays, which indicates that the particles in β -rays are much lighter than those in α -rays.

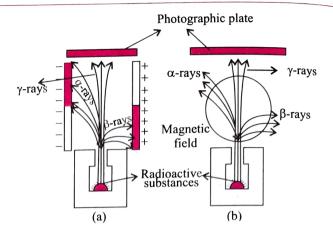


Fig. 6.1 (a) Deflection of radioactive rays in electric field, and
(b) Emission of radioactive rays and their deflection in magnetic
field

Some important properties of the three types of radiations $(\alpha$ -, β -, and γ -rays) are discussed below:

a. Alpha (α) rays

- i. Nature: The direction of the deflection of α -rays in electric and magnetic field shows that they carry positive charge. It is found that each α -particle carries two units of positive charge and has mass nearly four times that of hydrogen atom. Thus, α -particles are fast moving helium nuclei ${}_2^4\text{He}^{2+}$ with energy about $(6-16) \times 10^{-13}$ J.
- ii. Velocity: The velocity of α -rays is found to be nearly 1/10th to 1/20th of that of light, depending upon the kind of nucleus from which they are emitted.
- iii. Penetrating power: Since α -particles are heavy particles, hence they have small penetrating power. They are stopped by a piece of aluminium foil of 0.1 mm thickness.
- iv. Ionizing power: α -rays ionize the gas through which they pass. The ionization is due to the knock out of electrons from the molecules of the gas when the high-speed heavy α -particles hit these molecules. α -rays have 100 times greater ionizing power than β -rays and 10000 times greater than γ -rays.
- v. Effect on photographic plate and zinc sulphite screen: α-rays affect the photographic plate and produce luminescence on ZnS screen due to high kinetic energy.

b. Beta (β) rays

- i. Nature: The direction of the deflection of β -rays in electric and magnetic field shows that they carry negative charge. β -rays are merely electrons of energies that are about $(0.03-5.0) \times 10^{-13}$ J. β -rays are represented as $_{-1}\beta^0$ or $_{-1}e^0$.
- ii. Velocity: Since β -particles are much lighter than α -particles, they travel much faster. The velocity is 3% to 99% of that of light.
- iii. Penetrating power: β -rays are more penetrating than α -particles. This is due to small size and high velocity. It can penetrate to 1-cm-thick sheets of aluminium.

- Jonizing power: The ionizing effect of β-rays is about same as that of α -rays, but it is effective over much longer distance.
- Effect on photographic plate and zinc sulphite screen: β-rays affect the photographic plate and is greater than α-particles. It has little effect on ZnS screen due to low kinetic energy.
- _{ι Gamma} (γ) rays
- Nature: γ-rays are not deflected in electric or magnetic field showing that they do not carry charge. These rays are of very short wavelength and therefore are of very high energy.
- ii. Velocity: They travel with the same velocity as that of light.
- ii. Penetrating power: They have highest penetrating power out of all the three types of radiation. Their penetrating power is about 10^{10} times more than α -rays. They can be stopped only by thickness of about 15-20 cm of lead.
- iv. Ionizing power: As they do not have charge, their ionizing power is very low.
- v. Effect on photographic plate and zinc sulphite screen: y-rays have very little effect on the photographic plate and zinc sulphite screen.

The various properties of α -, β -, and γ -rays are given in Table. 6.1.

Table 6.1 Properties of α -, β -, and γ -rays

	Property	α-rays	β-rays	γ-rays
	Name	Fast moving He nuclei	Fast moving electrons	Electromagnetic radiations with very high frequency
b.	Notation	₂ He ⁴	$_{-1}e^{0}$	γ
	Charge	2 units (+ve)	1 units (-ve)	No charge
d.	Velocity	1/10 of light	3% to 90% of	Same as
			light	light waves
ŧ,	Nature of path	Straight line	Crooked	Waves
ſ.	Relative penetrating power	1 (or 0.01 mm of Al foil)	100 (or 0.1 cm of Al foil)	10000 (8 cm lead or 25 cm steel)
g.	ionizing power	10000	100	1
h	Deflection towards electrical or magnetic field	Deflected towards –ve pole	Deflected towards +ve pole	Not deflected
	influence			

6.4 METHODS TO DETECT/COUNT RADIOACTIVE RADIATIONS

There are two main radiation counters in practice:

a. Geiger Muller counter: It is used to count charged particles, e.g., α - and β -particles emitted by a radioactive nuclei. This counter is simply a metal tube filled with a gas such as argon. In order to count and detect neutrons, boron trifluoride (BF₃) is added along with gas in the GM counter. Neutron strikes $_5B^{10}$ nuclei to produce α -particle, which is then detected and counted in Geiger counter.

$$_{5}B^{10} + {_{0}}n^{1} \longrightarrow {_{3}}Li^{7} + {_{2}}He^{4}$$

b. Scintillation counter: γ-radiations are detected by scintillation counter. A phosphor is used in this counter which produces flash of light when it is struck by electromagnetic radiation such as γ -rays for detection of γ -rays. Sodium iodide (NaI) and thallium iodide (TII) is used as phosphor. Rutherford first of all used zinc sulphide (ZnS) as phosphor in the detection of α -particles.

6.5 NUCLEAR STRUCTURE AND NUCLEAR PROPERTIES

An atom of any element consists of a positively charged nucleus surrounded by one or more negatively charged electrons, the whole atom as such being electrically neutral. Nearly all the mass of an atom is concentrated in the nucleus, which has a radius of about 10^{-15} m, i.e., about 10^{-5} times that of the atom. The nucleus consists of positively charged protons and electrically neutral neutrons, collectively known as nucleons. The atomic number Z of an atom is the number of protons in the nucleus that defines the identity of an atom. The mass number A of an atom is the integer nearest to the relative atomic mass and is equal to the number of nucleons in the nucleus; it follows that the number of neutrons in the same nucleus is (A - Z). (a particular nuclear species with specific atomic number and a mass number referred to as *nuclide*).

Note: The area of cross-section of a nuclei is expressed in terms of a unit called barn (1 barn = 10^{-24} cm² or 10^{-28} m²).

Isotopes

- Atoms of same element having same atomic number but different mass number are known as isotopes, e.g., sO16, $_{8}O^{17}$, $_{8}O^{18}$.
- Isotopes of an element have different number of neutrons.
- Isotopes of an element are placed at same position in periodic
- Isotopes have different physical nature (due to different atomic mass) for same chemical nature (due to same atomic number).
- Nuclides and their decay products after one α and two β-particles are called isotopes.

$$z^{A^m} \xrightarrow{-\alpha} z^{-2} B^{m-4} \xrightarrow{-\beta} z^{-1} C^{m-4} \xrightarrow{-\beta} z^{A^m-4}$$

- Isotopes differ in radioactive nature and chemical reactivity.
 - Heavier isotopes may be radioactive.
 - Lighter isotopes are more reactive.

Therefore, $_1H^3$ is radioactive and $_1H^1$ is more reactive.

Isobars

 Atoms of different elements having same mass number are isobars, e.g., ₁₈Ar⁴⁰, ₁₉K⁴⁰, ₂₀Ca⁴⁰.

- Isobars have same number of nucleons.
- Isobars have different physical and chemical nature.
- Nuclides and their decay product after β emission are called isobars. Tritium, a β emitter forms isobar $_2\text{He}^3$.

$$_1H^3 \longrightarrow _2He^3 + _{-1}e^0$$

Isotones

- Atoms having same number of neutrons are called isotones, e.g., $_1H^2$ and $_2He^3$
- Mass number Atomic number = Constant (i.e., number of neutrons)

Isoelectronics

- Atoms and ions having same number of electrons are called as isoelectronics, e.g., N^{3-} , O^{2-} , F^{1-} , Ne, Na^{\oplus} , Mg^{2+} ,
- The size of isoelectronic ions decreases with increase in atomic number.

Isodiaphers

- · Atoms having same difference of neutron and proton or same isotopic number.
- Nuclides and their decay product after α emission are called isodiaphers.

e.g.,
$$_{Z}A^{m} \xrightarrow{-\alpha} _{Z-2}He^{m-4}$$

Isotopic number = n - p = m - 2Z

$$p = Z$$

$$p = Z - 2$$

$$n = m - Z$$

$$n = m - Z - 2$$

$$n - p = m - 2Z \qquad \qquad n - p = m - 2Z$$

$$n - p = m - 27$$

Isosters

 Molecules having same number of atoms and same number of electrons are called isosters, e.g., CO₂ and N₂O.

Nuclear isomers

- Nuclides having identical atomic number and mass number but differing in radioactive decay are known as nuclear isomers.
- · Nuclear isomers differ in their energy state, spins, and parities, e.g., Co^{60} and Co^{60m} ; Z^{69} and Zn^{69m} ; Br^{80} and Br^{80m} ;

The symbol m with mass number represents the metastable state of parent element.

$$Co^{60m} \xrightarrow{Isomeric} Co^{60}$$

 Nuclear isomers thus have different rate of decay, decay constant, half life, average life, and binding energy.

Packing fraction: The difference between actual isotopic mass and mass number is termed as packing fraction (Aston). Actual isotopic mass is not a whole number whereas mass number is a whole number.

Packing fraction

$$= \frac{Actual\ isotopic\ mass-Mass\ number}{Mass\ number} \times 10^4$$

The value of packing fraction depends upon the manner of packing of the nucleons within the nucleus. Its value can be negative, positive, or even zero.

Carbon¹² has zero packing fraction because it is taken as a reference on the atomic scale and its actual isotopic mass (12) is equal to its mass number (12).

The negative sign of the packing fraction means that the actual isotopic mass is less than the mass number. This in turn indicates that some mass has been transformed into energy (binding energy) during the formation of the nucleus. Such nuclei are, therefore, more stable.

The positive packing fraction should imply the opposite, i.e., the nuclei of such isotopes should be unstable. However, this generalization is not strictly correct especially for elements of low mass numbers. For these elements, though packing fraction is positive, yet they are stable. This is explained on the basis that the actual masses of protons and neutrons (of which nuclei are composed) are slightly greater than unity.

In general, lower the packing fraction, greater is the binding energy per nucleon and hence greater is the stability. The relatively low packing fraction of He, C, and O implies their exceptional stability. Packing fraction is least for Fe (-ve) and highest for for H(+78).

Meson theory of nuclear forces: Neutron is found to play a leading role in binding the nuclear particles. It has been established that neutron-proton attractions are stronger than the proton-proton or neutron-neutron attractions.

This is evident by the fact that deuteron, H² having one proton and one neutron, is quite stable while no particle having either two neutrons or two protons is known.

Yukawa in 1935, put forward a postulate that neutrons and protons are held together by very rapid exchange of nuclear particles called pi mesons (of the formation of a covalent bond by sharing of electrons). Pi mesons have mass equal to 275 times of the mass of an electron and a charge equal to +1, 0 or -1. These are designated as π^{\oplus} , π and π^{\odot} , respectively. The nuclear forces called into play by this rapid exchange of pi mesons between nucleons are also called exchange forces.

The binding forces between the unlike nucleons (p and n)are explained by the oscillation of charged pi meson $(\pi^{\oplus} \text{ or } \pi^{\ominus})$.

a.
$$p_1 + n_2 \rightleftharpoons n_1 + \pi^{\oplus} + n_2 \rightleftharpoons n_1 + p_2$$

b.
$$p_1 + n_2 \rightleftharpoons p_1 + \pi^{\odot} + p_2 \rightleftharpoons n_1 + p_2$$

Binding forces between like particles (p-p or n-n)result from the exchange of neutral mesons (π) as represented below.

c.
$$p_1 \rightleftharpoons p_1 + \pi^0 \text{ or } p_1 + \pi^0 \rightleftharpoons p_2$$

d.
$$n_1 \rightleftharpoons n_2 + \pi^0 \text{ or } n_1 + \pi^0 \rightleftharpoons n_2$$

6.6 GROUP DISPLACEMENT LAW

The atomic nuclei of radioactive elements are unstable and liable to disintegrate. During disintegration, atoms of new element alled daughter elements having different chemical and physical than the parent element (that has undergoes than the parent element) daugnes than the parent element (that has undergone decay)

pur into existence. The disintegration process (decay process) may proceed in

he following ways: ^β α -particle emission: When an α -particle [$_2$ He⁴] is emitted from the nucleus of an atom of the parent element, the from the new element, called the daughter element, nucleus of the new element, called the daughter element, possesses atomic mass number less by four units and pusses and a sum of the daughter elements after α -emission are called an isodiaphers of parent element.

Parent element $\xrightarrow{-\alpha}$ Daughter element

Atomic mass
$$A$$
 $A-4$

Atomic number Z $Z-2$

Examples are: ${}_{88}\text{Ra}^{226} \longrightarrow {}_{86}\text{Rn}^{222} + {}_{2}\text{He}^4$
 ${}_{92}\text{U}^{218} \longrightarrow {}_{90}\text{Th}^{234} + {}_{2}\text{He}^4$
 ${}_{84}\text{Po}^{215} \longrightarrow {}_{82}\text{Pb}^{211} + {}_{2}\text{He}^4$

It may be pointed out that there is conservation of both atomic number and atomic mass number in the equation of a nuclear reaction.

b. β-emission: β-particle is merely an electron which has negligible mass. When a beta particle is emitted, the nucleus of the new element formed possesses the atomic mass, but nuclear charge or atomic number is increased by 1 unit over the parent element. Beta particle emission is due to the result of decay of neutron into proton and electron.

$$_{0}n^{1}\longrightarrow {}_{1}P^{1}+{}_{-1}e^{0}$$

Parent element $\xrightarrow{-\beta}$ Daughter element

Atomic mass

$$\boldsymbol{A}$$

Atomic number

$$Z+1$$

 \boldsymbol{Z} β -emission results to daughter element that is an isobar of parent element.

Examples are:
$${}_{82}\text{Pb}^{214} \longrightarrow {}_{83}\text{Bi}^{214} + {}_{-1}e^0$$

 ${}_{90}\text{Th}^{234} \longrightarrow {}_{91}\text{Pa}^{234} + {}_{-1}e^0$
 ${}_{83}\text{Bi}^{213} \longrightarrow {}_{84}\text{Po}^{213} + {}_{-1}e^0$

c. γ-emission: Gamma rays are emitted due to secondary effects. After the emission of an alpha particle or beta particle, the nucleus is left behind in excited state due to recoil. The excess of energy is released in the form of gamma rays. Thus, γ -rays arise from energy re-arrangements in the nucleus. As γ-rays are short wavelength electromagnetic radiations with no charge and no mass, their emission from a radioactive element does not produce a new element.

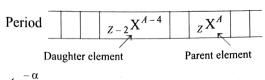
In case an α -emission is followed by two successive β-emissions, a nuclide which is isotopic with the original one may be produced, e.g.,

one may be produced, e.g.,

$$_{92}U^{238} \xrightarrow{-\alpha} _{90}Th^{234} \xrightarrow{-\beta} _{91}Pa^{234} \xrightarrow{-\beta} _{92}U^{234}$$

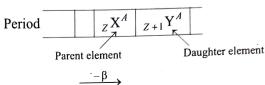
The above results have been summarized below as "group displacement law":

i. When an α -particle is emitted, the new element formed is displaced two positions to the left in the periodic table than that of the parent element.



Two positions left of the original element.

ii. When a β -particle is emitted, the new element formed is displaced one position to the right in the periodic table than that of the parent element.



One position right of the original element

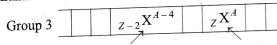
However, the group displacement law does not apply on lanthanides and actinides.

The lanthanides and actinides are in group 3, so after α and β emission, the daughter element remains in the same group (except for La, Ac, and last element Lu and Lr), i.e., all in third group.

For example, in α -emission from $_{59}Pr^{141}$ \longrightarrow

 $_{58-2}$ $X^{141-4} + _{2}$ He⁴, the daughter element X also remains in third group.

Lanthanide series



Daughter element

Both parent element and daughter element are in third group.

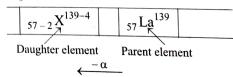
Similarly, β -emission from $_{59}\text{Pr}^{141} \rightarrow _{59+1}\text{Pr}^{141} + _{-1}e^0$ 59 Pr¹⁴¹ 60 X¹⁴¹ Group 3

Parent element

Here again parent and daughter elements remain in same

But in the case of ₅₇La¹³⁹ element α-emission shift, the daughter element shift by two position left in the periodic table. But β-emission from La produces daughter element that belongs to group 3.

For example, α -emission



Two position left of the original element

Similarly, in the α - and β -emission from actinides series, the daughter element remains in the same group except for Ac and Lr.

In addition to α -, β -, and γ -emissions, two other types of decay processes are also observed, viz, $\beta^\oplus\text{-emission}$ and **a.** β^{\oplus} -emission: A positively charged beta particle (β^{\oplus}) is known as *positron*. The emission of a positron (β^{\oplus}) results into a decrease of atomic number by one unit. It is now believed that β -emission involves the transformation within the nucleus of a neutron to proton or proton to neutron.

Thus

$$_{0}n^{1} \rightarrow {}_{1}H^{1} + {}_{-1}e^{0} (n \rightarrow p + p^{\oplus}); {}_{1}H^{1} \rightarrow {}_{0}n^{1} + {}_{+1}e^{0}$$
 (Positron)

An example of β^{\oplus} emission is ${}_{11}\text{Na}^{22} \longrightarrow {}_{10}\text{Ne}^{22} + {}_{+1}e^0 (\beta^{\oplus})$ ${}_{7}\text{N}^{13} \longrightarrow {}_{6}\text{C}^{13} + \beta^{\oplus} \text{ or } {}_{+1}e^0$

b. K-capture: In some nuclides, the nucleus may capture an electron from the K shell. The vacancy created is filled by electrons from higher levels giving rise to characteristic X-rays.

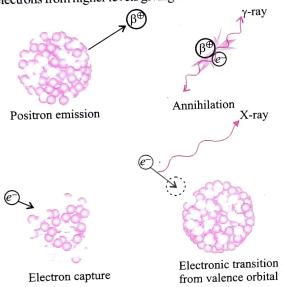


Fig. 6.2 $\beta^\oplus\text{-emission}$ and K-capture of electron

This process is known as K-electron capture or simply K-capture. An example of K-capture is:

Recapture: A strong that
$$S_{56}$$
 Ba¹³³ + $S_{-1}e^0 \longrightarrow S_5$ Cs¹³³ + X-ray

The change in the nucleus is represented by $p^{\oplus} + e^{\ominus} \longrightarrow n$

The neutron produced remains in the nucleus and the atomic number decreases by one unit as the result of K-capture.

ILLUSTRATION 6.1

What may be the place of a daughter element in the periodic table, which is obtained after the nuclide $_{84}\text{Po}^{218}$ undergoes an α -emission followed by two successive β -emissions?

Sol. The lose of one α -particle will reduce the mass number by 4 and atomic number by 2. Subsequent two β° emissions will increase the atomic number by 2 without affecting the mass number. Hence, the new element will be only an isotope of the parent nuclide with mass number four less, i.e., $_{84}\text{Po}^{214}$, and hence its position in the periodic table remains unchanged.

ILLUSTRATION 6.2

In the decay series $_{92}U^{238}$ to $_{82}Pb^{206}$, how many α -particles and how many β^{\odot} -particles are emitted?

Sol. The change in mass is 238 - 206 = 32 units. It means that 32/4 = 8 α -particles are emitted. With the emission of 8 α -particles, the change in atomic number will be $8 \times 2 = 16$, i.e., the new element would have atomic number 92 - 16 = 76. But the final product Pb has atomic number 82. It means there would have been an emission of 82 - 76 = 6 β -particles.

ILLUSTRATION 6.3

When nucleus of an electrically neutral atom undergoes a radioactive decay process, it will remain neutral after the decay if the process is

- a. An α-decay
- b. A β[⊕]-decay
- c. A γ-decay
- d. A K-capture process

Sol.

c. Since γ-particles are neutral, therefore, its decay will not change the charge of atom.

ILLUSTRATION 6.4

Arrange in increasing order of:

- a. The mass of α , β , and γ
- **b.** The penetration power of α , β , and γ
- c. The speed of α , β , and γ
- d. The ionization capacity of gases of α , β , and γ

Sol.

a. Increasing order of mass

$$\gamma < \beta < \alpha$$

b. Penetration power of α , β , and γ

$$\alpha < \beta < \gamma$$

c. Speed of particles

$$\alpha < \beta < \gamma$$

d. Ionization capacity

$$\gamma < \beta < \alpha$$

ILLUSTRATION 6.5

α-rays have ionization power because they possess

- a. Lesser kinetic energy
- b. Higher kinetic energy
- c. Lesser penetration power
- d. Higher penetration power

Sol.

b. Because of higher kinetic energy α -rays have ionization power.

Calculate the number of neutrons in the remaining atoms after the emission of an alpha particle from $_{92}U^{238}$ atom.

Sol. Parent element = $_{92}U^{238}$

On account of emission of an alpha particle, the atomic mass is decreased by 4 units and atomic number by 2 units.

Number of neutrons = Atomic mass – Atomic number =
$$234 - 90 = 144$$

ILLUSTRATION 6.7

The atomic mass of thorium is 232 and its atomic number is 90. During the course of its radioactive disintegration 6α and 4β particles are emitted. What is the atomic mass and atomic number of the final atom?

Radioactive disintegration reaction:

$$_{\text{on}} \text{Th}^{232} \xrightarrow{-6\alpha, -4\beta} Z$$

Loss of $\alpha\text{-particle}$ decreases the atomic mass

$$= 6 \times 4 = 24 \text{ unit}$$

So atomic mass of the product atom = (232 - 24) = 208

Also α -particle decreases the atomic number of element by

2. Therefore, total loss of atomic number = $6 \times 2 = 12$

Loss of β -particle does not change the atomic mass but loss of β -particle increases the atomic number by 1.

Therefore, total gain of atomic number due to β -particle = 4

The total change in atomic number = Loss due to α -particle emission

- Gain due to β particle emission

$$= 12 - 4 = 8$$

So, atomic number of product atom = 90 - 8 = 82

Therefore, Z has atomic mass = 208

Atomic number = 82

or 82Z208

ILLUSTRATION 6.8

Aradioactive element A disintegrates in the following manner:

$$A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D$$

Which one(s) of the elements A, B, C, and D are isotope(s) and which one(s) is/are isobar(s)?

Let the mass number and atomic number of element A be *M* and *Z*, respectively. The following changes shall occur during disintegration:

$$z^{AM} \xrightarrow{-\alpha} z_{-2}B^{M-4} \xrightarrow{-\beta} z_{-1}C^{M-4} \xrightarrow{-\beta} z^{D^{M-4}}$$
A and D are isotopes as both have same value of Z.

B, C, and D are isobars as these have same values of atomic mass.

ILLUSTRATION 6.9

How many moles of helium are produced when 1 mole of ₉₂U²³⁸ disintegrates into ₈₃Pb²⁰⁶?

Sol. Radioactive change is

$$_{92}U^{238} \longrightarrow _{82}Pb^{206}$$

Decrease in mass =
$$(238 - 206) = 32$$

Let the number of α -particles emitted be x.

$$4x = 32$$
 \Rightarrow $x = 8$

Thus, 8 moles of helium are produced when 1 mol of $_{92}$ U²³⁸ disintegrates into $_{82}$ Pb²⁰⁶.

ILLUSTRATION 6.10

How many α - and β -particles will be emitted when $_{90}\text{Th}^{234}$ changes into $_{84}\text{Po}^{218}$?

Sol. The change is:

$$_{90}\text{Th}^{234} \longrightarrow {}_{84}\text{Po}^{218}$$

Parent End product

Decrease in mass = (234 - 218) = 16 amu

Mass of 1 α -particle = 4 amu

Therefore, number of α -particles emitted = $\frac{16}{4}$ = 4

Number of β-particles emitted

= $2 \times \text{Number of } \alpha\text{-particles emitted } - (\text{Atomic number } \text{of parent} - \text{Atomic number of end product})$

$$= 2 \times 4 - (90 - 84) = (8 - 6) = 2$$

Hence, number of α -particles = 4

and number of β -particles = 2

ILLUSTRATION 6.11

Calculate the number of α - and β -particles emitted when $_{92}U^{238}$ changes into radioactive $_{82}Pb^{206}$.

Sol. Parent element = $_{92}$ U²³⁸; daughter element = $_{82}$ Pb²⁰⁶

Let $x \alpha$ - and $y \beta$ -particles be given out during the change

$$_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + x_2He^4 + y_{-1}e^0$$

Equating mass number on both sides

$$238 = 206 + 4x + y \times 0$$

or
$$x = 8$$

Equating atomic number on both sides

$$92 = 82 + 2x + v(-1)$$

$$= 82 + 2 \times 8 + \nu(-1)$$

or
$$y = 0$$

 \therefore Number of α -particles = 8; Number of β -particles = 6

ILLUSTRATION 6.12

If a $_{92}U^{235}$ nucleus upon being struck by a neutron changes to $_{56}Ba^{145}$, three neutrons and an unknown product. What is the unknown product?

...(i)

$$_{92}U^{235} + _{0}n^{1} \longrightarrow {}_{56}Ba^{145} + _{Z}X^{A} + 3_{0}n^{1}$$

Equating the mass number on both sides, we get

$$235 + 1 = 145 + A + 3 \times 1$$

 $\therefore A = 88 = \text{Atomic mass of X atom}$

Similarly, equating atomic numbers on both sides, we get

$$\therefore 92 + 0 = 56 + Z + 3 \times 0$$

 \therefore Z = 36 = Atomic number of X atoms

Therefore, unknown product is $_{36}X^{88}$, i.e., $_{36}Kr^{88}$.

ILLUSTRATION 6.13

 $_{90}$ Th 232 belongs to III group. It emits an lpha-particle. The daughter element belongs to

Sol.

b.
$${}_{90}\text{Th}^{232} \longrightarrow {}_{88}\text{Ra}^{228} + {}_{2}\text{He}^4;$$

Note that elements from 89 to 103 are placed in group III.

ILLUSTRATION 6.14

A heavier element continuously emits α - and β -particles. The finally stable element may belong to:

Sol.

a. Neptunium series ends at Bi (15th group) and rest all series terminate at Pb (14th group).

ILLUSTRATION 6.15

Radioactive disintegration of 88 Ra²²⁶ takes place in the following manner into RaC.

$$Ra \xrightarrow{-\alpha} Rn \xrightarrow{-\alpha} RaA \xrightarrow{-\alpha} RaB \xrightarrow{-\beta} RaC$$

Determine the mass number, atomic number, and group of periodic table for RaC.

Sol. Parent element is 88 Ra²²⁶.

Atomic mass = 226

Atomic number = 88

Emission of an α shows a loss in mass number by 4 units and loss in atomic number by 2 units.

Emission of a β shows a gain in atomic number by one unit; mass number remains same.

$$\begin{array}{c} \text{Ras} & \text{Ra}^{226} \xrightarrow{(-_2\text{He}^4)} \\ \text{88} & \text{Ra}^{226} \xrightarrow{(-_2\text{He}^4)} \\ \text{II group} & \text{Zero group} & \text{VI group} \end{array} \xrightarrow{\text{VI group}} \begin{array}{c} \text{85} & \text{RnB}^{218} \\ \text{VI group} & \text{VII group} \end{array}$$

Atomic number of RaC = 83

Mass number of RaC = 214

Group of element RaC is V from configuration 2, 8, 18, 32, 18, 5.

The number of electrons in outer shell suggest for group V

ILLUSTRATION 6.16

An atom has atomic mass 232 and atomic number 90. During the course of disintegration, it emits 2 β-particles and few α-particles. The resultant atom has atomic mass 212 and atomic number 82. How many α-particles are emitted during this process?

Sol. Let the reaction is

$$_{90}A^{232} \longrightarrow _{82}B^{212} + x_2He^4 + 2_{-1}e^0$$
 ...(i)

Let x be the number of alpha particles emitted equate the atomic mass of both side of Eq. (i),

$$232 = 212 + 4x + 2 \times 0$$

$$\therefore x = \frac{232 - 212}{4} = 5$$

Therefore, 5 α-particles are emitted.

ILLUSTRATION 6,17

 $_{92}U^{238}$ is a natural α -emitter. After α -emission the residual nucleus U_{X1} in turn emits a β -particle to produce another nucleus U_{x2} . Find out the atomic number and mass number of U_{x_1} and U_{x_2} .

Sol. Parent element = $_{02}U^{238}$

After α-emission, the daughter nucleus formed is U_{x1}. The reaction is:

$$_{92}U^{238} \longrightarrow _{Z}U_{X1}^{A} + _{2}He^{4}$$

Equating atomic mass on both sides, we get

$$238 = A + 4$$

$$A = 234$$

Equating atomic mass on both sides, we get

$$92 = Z + 2$$

$$\therefore Z = 90$$

The product atom is 90U234X1. This product atom emits β-particle.

$$_{90}U^{234} \longrightarrow {}_{Z}U^{A}_{X2} + {}_{-1}e^{0}$$

Solving for atomic mass, we get A = 234

Solving for atomic number, we get Z = 91

Therefore, the product atom is $_{91}U_{X2}^{234}$.

ILLUSTRATION 6.18

A radioactive nuclide emits y-rays due to

- K-electron capture
- b. Nuclear transition from higher to lower energy
- Presence of greater number of neutrons than protons
- Presence of greater number of protons than neutrons

Sol

V group

b. After α -, β -emission, nucleus goes to excited state; when it returns to normal state, emission of y-radiations takes place.

 β which of the following transformations, the β -particles are

- B. Proton to neutron
- b. Neutron to proton
- c. Proton to proton
- d. Neutron to neutron



$$b_{0}n^{1} \longrightarrow {}_{1}H^{1} + {}_{-1}e^{0} + antineutrino$$

ILLUSTRATION 6.20

During the transformation of cXa to dYb, the number of B-particles emitted are

a.
$$d + \left(\frac{a-b}{2}\right) - c$$
 b. $\frac{a-b}{4}$

b.
$$\frac{a-b}{4}$$

c.
$$d + \left(\frac{a-b}{2}\right) + c$$
 d. $2c - d + a - b$

d.
$$2c - d + a - l$$

a. For transformation of
$$_{c}X^{a} \longrightarrow {}_{d}Y^{b} + x_{2}He^{4} + \beta$$

Number of
$$\alpha$$
-particles emitted = $\frac{a-b}{4}$

Equating for atomic number on both sides, we get

$$c = d + 2\left(\frac{a-b}{2}\right) + \beta (-1)$$

or
$$\beta = d + \frac{a-b}{2} - c$$

LLUSTRATION 6.21

Which of the following elements is an isodiapher of 92U235?

a.
$$_{82}$$
Pb²¹² **b.** $_{90}$ Th²³¹ **c.** $_{83}$ Bi²⁰⁹ **d.** $_{91}$ Pa²³¹

d.
$$_{01}$$
Pa²³¹



c. Isodiaphers are formed by α -emission

$$_{92}U^{235} \longrightarrow _{90}Th^{231} + _{2}He^{4}$$

ILLUSTRATION 6.22

In the radioactive decay

$$z^{X^A} \rightarrow {}_{Z+1}Y^A \longrightarrow {}_{Z-1}Z^{A-4} \rightarrow {}_{Z-1}Z^{*A-4}$$

The sequence of emission is

a.
$$\alpha$$
, β , γ

c.
$$\beta$$
, α , γ **d.** β , γ , α

c.
$$_{Z}X^{A} - _{-1}e^{0} \rightarrow _{Z+1}Y^{A}$$

 $_{Z+1}Y^{A} - _{2}He^{4} \rightarrow _{Z-1}Z^{A-4}$
 $_{Z-1}Z^{A-4} - \gamma \rightarrow _{Z-1}Z^{*A-4}$

ILLUSTRATION 6.23

In the sequence of the reaction

 $A \xrightarrow{-\beta} B \xrightarrow{-\beta} C \xrightarrow{-\alpha} D$, what is the relationship between D and A?

Nuclear Chemistry 6.11

Sol. From transformation of $A \xrightarrow{-\beta} B \xrightarrow{-\beta} C \xrightarrow{-\alpha} D$, the changes in mass number and atomic number is:

$$r^{A^X} \xrightarrow{-\alpha} r_{+1} B^X \xrightarrow{-\beta} r_{+2} C^X \xrightarrow{-\alpha} r^{D^{X-4}}$$
Therefore, the atomic number is:

Therefore, the atomic number of A and D is same. Hence, it is an isotope.

ILLUSTRATION 6.24

The radiations from a naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are

- a. Only α-rays
- b. Only β-rays
- c. Both α and β -rays
- d. Either α- or β-rays

Sol.

d. Both α - and β -particles deflect in opposite direction in the presence of magnetic field. Here only one deflection is observed that will be for either α- or β-rays.

ILLUSTRATION 6.25

Which of the following radiations is most easily stopped by air?

- a. α-rays
- b. γ-rays
- c. B-rays
- d. X-rays

Sol.

a. α -rays have less penetrating power.

ILLUSTRATION 6.26

K-capture

- a. Refers to capture by other nucleus of an electron from
- **b.** Results in decrease in Z
- c. Is of the type

$$_{56}Ba^{133} + _{-1}e^0 \longrightarrow _{55}Cs^{133} + \gamma$$
-rays

- d. All of these
- Sol. d.

ILLUSTRATION 6.27

The decay of a neutron to a proton also yields

- $\mathbf{a}_{-1}e^0$ $\mathbf{b}_{-1}e^0$ $\mathbf{c}_{-1}H^2$
- **d.** ,He⁴

Sol.

a.
$$_{0}n^{1} \longrightarrow {}_{1}H^{1} + {}_{-1}e^{0}$$

CONCEPT APPLICATION EXERCISE 6.1

- 1. From the following nuclear reaction
 - Po $\xrightarrow{-\alpha}$ Pb $\xrightarrow{-\beta}$ Bi, predict the group of the elements Po and Bi if you know that Pb belongs to group 14 of the periodic table.
- 2. After the emission of an α -particle from the atom of $_{92}U^{238}$, what is the number of neutrons left in the atom?

3. Match the following:

a. Isotopes

 \mathbf{p} . ${}_{\circ}\mathrm{O}^{16}$ and ${}_{\circ}\mathrm{O}^{17}$

b. Isobars

q. Na[⊕], Mg²⁺, F[⊙]

c. Nuclear isomers

 \mathbf{r} . $_{1}\mathrm{H}^{2}$ and $_{2}\mathrm{He}^{3}$

d. Isosters

s. U_4 and U_7

e. Isotones

t. CO₂ and N₂O

f. Isoelectronics

u. ${}_{A}X^{Z}$, ${}_{A-2}X^{Z-4}$

g. Isodiaphers

 $v_{.20}$ Ca⁴⁰ and $_{10}$ K⁴⁰

4. How many α - and β -particles will be emitted by $_{88}Ra^{226}$ in changing to a stable isotope of 82Pb206?

5. How many α -, β -particles will be emitted when $_{90}\text{Th}^{234}$ changes to 86Rn²²²?

6. What is the effect of temperature and pressure on the rate of radioactive disintegration?

7. Name the most radioactive element isolated from pitchblende?

8. In the sequence of following reaction

 $A \xrightarrow{-\beta} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D$, what is the relationship between D and A?

9. An unstable isotope of carbon has n/p ratio of 1.33 times greater than the stable element and is moving with a velocity v of 6.023 m s⁻¹. What is the value of $\frac{h}{22} \times 10^{+26}$ in SI units?

ANSWERS

1. Po: Group 16; Bi: Group 15

3. $a \rightarrow p$; $b \rightarrow v$; $c \rightarrow s$; $d \rightarrow t$; $e \rightarrow r$; $f \rightarrow q$; $g \rightarrow u$

4. α-particles: 5, β-particles: 4

5. α-particles: 3, β-particles: 2

6. No effect

7. Radium

8. A and D are isobars

9. 7

6.7 NUCLEAR STABILITY AND **NEUTRON/PROTON RATIO**

It has been found that the nuclei of those atoms are stable whose ratio of the neutrons to protons (n/p) ratio lies in the range of 1-1.5.

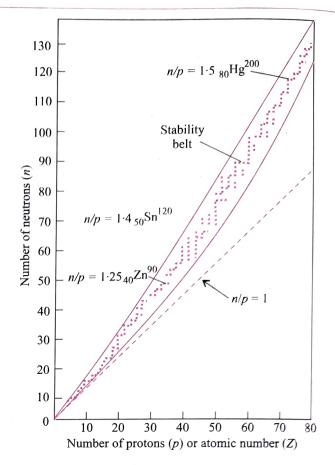
The variation of n versus p for some nuclei is shown in Fig. 6.3.

The stable nuclei lie within the shaded area which is called the region or zone of stability. All the nuclei falling outside this zone are invariably radioactive and unstable in nature. Nuclei that fall above the stability zone have an excess of neutrons while those lying below have more protons. Both of these cause instability. These nuclei attain stability by making adjustment in the N/P ratio. Two cases thus arise:

a. n/p ratio is higher than required for stability: Such nuclei have the tendency to emit β-rays, i.e., transforming a neutron into proton.

$$_{0}n^{1} \longrightarrow _{1}p^{1} + _{-1}e^{0}$$

(\beta-particle)



A plot of number of neutrons (n) against the atomic number (Z) for a range of stable nuclei

Thus, in β -emission n/p ratio decreases. For example, in the change of ${}_{6}C^{14}$ to ${}_{7}N^{14}$, n/p ratio decreases from 1.33 to 1. $_{6}C^{14} \longrightarrow {}_{7}N^{14} + {}_{-1}e^{0}$

b. n/p ratio is lower than required for stability: Such nuclei can increase n/p ratio by adopting any one of the following three ways:

i. By emission of an alpha particle (natural radioactivity)

$$_{92}U^{238} \longrightarrow _{90}Th^{234} + _{2}He^{4}$$
 (α -particle)
 n/p ratio 146/92 144/90
= 1.58 = 1.60

ii. By emission of a positron (artificial emission)

$$_{7}N^{13} \longrightarrow {}_{6}C^{13} + {}_{+1}e^{0}$$
 $_{n/p} \text{ ratio } 6/7 = 0.85 \qquad 7/6 = 1.16$

iii. By K-electron capture

$$_{79}Au^{194} + _{-1}e^0 \longrightarrow {}_{78}Pt^{194}$$
 $n/p \text{ ratio} \quad 115/79 = 1.45 \qquad \qquad 116/78 = 1.48$

From Fig. 6.3, it is clear that for stable nuclides up to Z = 20, n = 20(Ca⁴⁰), the relationship can be represented by a line with a slope of 45 degree, i.e., maximum stability is attained when n = Z. At higher values of Z, the graph becomes curved with the slope of the curve gradually increasing. To the right of the curve where the n/Z ratio is lower than that required for stability, a radioactive nuclide can decay by $\beta^{\oplus}\text{-emission}$ or gio of (n+1)/(Z-1). To the left of the curve, a radioactive gio of (n+1)/(Z-1). To the left of the curve, a radioactive gio of (n+1)/(Z-1). To the left of the curve, a radioactive gio of (n+1)/(Z-1). In the left of the curve, a radioactive gio of (n+1)/(Z-1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In either case, the daughter nuclide might be stable (n-1)/(Z+1). In eit

Effect of n/p ratio on nuclear stability

- _{a.} Nuclides which have an odd number of protons and odd number of neutrons are unstabled (i.e., radioactive) and which have *n/p* ratio not in stability zone.
- b. If the Atomic number is below 82, then when n/p ratio is very low, it increases either by β^{\oplus} ($_{+1}e^0$) emission or K-capture ($_{1}e^0$). The new n/p ratio of daughter element is $\left(\frac{n+1}{Z-1}\right)$. Here p changes to n and β^{\oplus} .

i.e.,
$$_{0}n^{1} \longrightarrow {}_{1}H^{1} + {}_{-1}e^{0}$$
.

c. If the atomic number is below 82, then when n/p ratio is very high, it decreases by $\beta^{\odot}(_1e^0)$ emission. The n/p ratio of the daughter element becomes $\left(\frac{n-1}{Z+1}\right)$. Here n changes to p and β^{\odot} .

$$_{0}n^{1}\longrightarrow {}_{1}H^{1}+{}_{-1}e^{0}.$$

- d. The changing of n/p ratio towards the stability of elements having atomic weight less than 82 is due to strong n-p and p-p attractive forces operating at nuclear distance.
- ϵ . If the atomic number is greater than 82, then when n/p ratio

becomes stable by a emission ($_2\text{He}^4$) leading to daughter element n/p ratio to $\left(\frac{n-2}{Z-2}\right)$.

- **f.** For heavier nucleus, (p-p) repulsion forces start to offset the attractive forces. Therefore, the reduction of Z leads to the reduction of p-p repulsion, and excess of neutrons over protons are required for stability.
- **g.** Up to $Z = 20 \longrightarrow \text{Stability value of } n/p = 1$

Up to
$$Z = 30 \longrightarrow$$
 Stability value of $n/p = 1.13$

Up to
$$Z = 40 \longrightarrow \text{Stability value of } n/p = 1.25$$

Up to
$$Z = 50 \longrightarrow \text{Stability value of } n/p = 1.40$$

Up to
$$Z = 60 \longrightarrow \text{Stability value of } n/p = 1.80$$

Up to
$$Z = 80 \longrightarrow$$
 Stability value of $n/p = 1.53$

When the value of Z becomes greater than 82 some nuclides attain greater stability (i.e., decay by α -emission) which reduces the initial n/Z value of (n-2)/(Z-2), the more important consequence being the reduction of Z leading to the reduction of p-p repulsions.

From the above discussion, it appears that, the neutron-proton ratio plays a vital role in deciding the stability of nuclides as also the kinds of decay they undergo.

6.8 RADIOACTIVE DECAY SERIES

Radioactive heavy nuclei decay by a series of α - and/or β -emissions, finally resulting in the formation of a stable isotope of lead. All the nuclei formed from initial to the final stable element constitute a *series*. There are four decay series distinguished by whether the mass numbers are divided by 4 or whether when divided by 4, there are remainders of 1, 2, or 3. The parent of (4n) is $_{90}$ Th 232 and its end product is $_{82}$ Pb 208 . The corresponding parents of the (4n+2) and (4n+3) series are $_{92}$ U 238 and $_{92}$ U 235 , respectively. An artificial series (4n+1) starts with neptunium $_{93}$ Np 237 and ends in $_{83}$ Bi 209 . These series are summarized in Table 6.2.

			Table	6.2 The decay seri	ies		
Series	Name of the series	Starting element	Stable end product	Value of <i>n</i> for the starting element	Value of <i>n</i> for the stable end product	Number of α particles emitted	Number of β particles emitted
4 <i>n</i>	Thorium series	₉₀ Th ²³²	₈₂ Pb ²⁰⁸	58	52	6	4
4n + 1	Neptunium series (artificial series)	$^{93}_{93}$ Np ²³⁷ or 94 Pu ²⁴¹	₈₃ Bi ²⁰⁹	59 60	52 52	7 8	5
4n + 2	Uranium series	₉₂ U ²³⁸	82Pb ²⁰⁶	59	51	8	6
4n+3	Actinium series	92 ^{U235} or	₈₂ Pb ²⁰⁷	58 56	51 51	7	4
		₈₉ Ac ²²⁷			31	5	3

Similarities between radioactive series

- a. In all the series, there is an element of zero group with atomic number 86. This element emits in the gaseous state and the process is called emanation. Different names are given to the three isotopes. These are *radon* in uranium series, *thoron* in thorium series, and *actinon* in actinium series.
- b. In all the series, the last product is an isotope of lead (atomic
- number 82): Pb²⁰⁶ in uranium series, Pb²⁰⁷ in actinium series, while Pb²⁰⁸ in thorium series. Due to this reason, lead is found in nature as a mixture of these three isotopes.
- c. In all the series, there are certain elements which disintegrate in a branching process by emitting either α- or β-particles. The species thus formed are then disintegrated in such a way so as to give a common product.

Table 6.3 Radioactive disintegration series

Thorium (4n) series	Neptunium (4n + 1) series	Uranium (4 <i>n</i> + 2) series	Actinium (4n + 3) series		
₉₀ Th ²³²	94Pu ²⁴¹	92 ^{U238}	92 ^{U235}		
- α	$-\beta$	- α	$-\alpha$		
88Ra ²²⁸	₉₅ Am ²⁴¹	₉₀ Th ²³⁴	90 Th ²³¹		
- β	$-\alpha$	- β	- β		
A - 228	$_{92}U^{237} \xrightarrow{-\beta} Np^{237}$	↓ ₉₁ Pa ²³⁴	↓ 91 Pa ²³¹		
89Ac ²²⁸			911 - a		
↓-β T1-228	$-\alpha$ $_{91}$ Pa ²³³	$ \begin{array}{c} $	89Ac ²²⁷		
90 Th ²²⁸			-a/\ \-\β		
$-\alpha$ 88 \mathbf{Ra}^{224}	$ \begin{array}{c} $	$ \begin{array}{c} -\alpha \\ 90 \text{Th}^{230} \end{array} $	$_{87}^{\checkmark}$ Fr ²²³ $_{90}$ Th ²²⁷		
			87 ¹¹ 90 111 -α -α		
$-\alpha$ 86 Rn^{220}	$\int_{90}^{-\alpha} Th^{229}$	$-\alpha$ 88 Ra^{226}	88Ra ²²³		
		88 \ \ - α	88 ¹ Cα		
$ \begin{array}{c} $	$-\alpha$ 88 Ra^{225}	86Rn ²²²	86 ^R n ²¹⁹		
$-\beta$ $-\alpha$	881 - β	86 ¹ - α	862 α		
$_{85}At^{216}$ $_{82}Pb^{212}$	89Ac ²²⁵	84Po ²¹⁸	$\frac{1}{84}$ Po ²¹⁵		
85 ¹ 10 82 ¹ 0 -β	89^{2} $\left -\alpha \right $	$-\beta$ $-\alpha$	841 σ		
83Bi ²¹²	87 ^F r ²²¹	$^{-\beta}_{85}$ At ²¹⁸ $^{-\alpha}_{82}$ Pb ²¹⁴	82Pb ²¹¹		
-α/ -β	$\left -\alpha\right $	$-\alpha$ β	82		
$_{81}\text{Tl}^{208}$ $_{84}\text{Po}^{212}$	$_{85}$ At ²¹⁷	$_{83}$ Bi ²¹⁴	83Bi ²¹¹		
$-\beta$ α	$-\alpha$	-α \ \-β	$-\alpha$ β		
82Pb ²⁰⁸	83Bi ²¹³	$_{81}\text{Tl}^{210}$ $_{84}\text{Po}^{214}$	81Tl ²⁰⁷ 84Po ²¹¹		
62	$-\alpha$ β	$-\beta$ $-\alpha$	$-\beta$ $-\alpha$		
	$_{81}\text{Ti}^{209}$ $_{84}\text{Po}^{213}$	82Pb ²¹⁰	82Pb ²⁰⁷		
	-β \α	- β	0.2		
	$^{82}Pb^{209}$	$_{83}$ Bi ²¹⁰			
	β	$-\alpha / -\beta$			
	$_{83}$ Bi 209	$\begin{array}{c c} & & & & \\ & & & & \\ & & & & \\ & & & & $			
		$-\beta$ α			
		82Pb ²⁰⁶			

9 NUCLEAR BINDING ENERGY

binding energy is the energy released during the pothetical formation of the nucleus by the condensation of or ndividual nucleon. Thus,

 $\frac{\text{Total binding energy per nucleon}}{\text{Binding energy per nucleons}} = \frac{\text{Total binding energy}}{\text{Number of nucleons}}$

For example, the mass of hydrogen atom is equal to the of the masses of a proton and an electron. For other atoms, the atomic mass is less than the sum of the masses of protons, me around and electrons present. This difference in mass, termed neurons defect, is measure of the binding energy of protons and as much mass—energy relationship postulated neutrons in the nucleus. The mass—energy relationship postulated by Einstein is expressed as:

$$\Delta E = \Delta mc^2 \qquad ...(i)$$

where ΔE is the energy liberated, Δm is the loss of mass, and c is the speed of light.

Consider a helium nucleus which contains 2 protons and Ineutrons; the mass of helium nucleus on ${}^{12}C = 12 \text{ m}_u$, scale is $4.0017 \,\mathrm{m}_{\mathrm{m}}$. The mass of individual isolated proton and neutron is 1,0073 and 1.0087 m_u, respectively. The total mass of 2 protons and 2 neutrons is $(2 \times 1.0073) + (2 \times 1.0087) = 4.0320 \text{ m}_{\text{n}}$. The loss in mass or the mass defect for helium nucleus is $4.0320 \, m_n - 4.0017 \, m_n = 0.0303 \, m_n$

Since 1 m_u = 1.66057 × 10⁻²⁷ kg and
$$c = 2.998 \times 10^8$$
 ms⁻¹
 $\Delta E = 0.0303 \times 1.66057 \times 10^{-27} \times 6.02 \times 10^{23}$
× $(2.998 \times 10^8)^2$ kg m² s⁻² mol⁻¹

=
$$2.727 \times 10^{12} \text{ J mol}^{-1}$$

Thus, the molar nuclear binding energy of helium nucleus He^4 is 2.73×10^{12} J mol⁻¹.

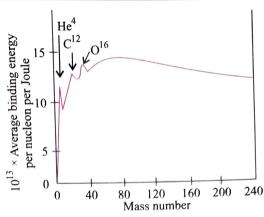
The binding energy of a nucleus is generally quoted as energy million electron volts (MeV) per nucleon. One million electron volts are equivalent to $9.6 \times 10^{10} \text{ J mol}^{-1}$. Thus, the formation of a helium nucleus results in the release of

$$2.7 \times 10^{12}$$
 /9.6 × 10^{10} MeV = 28 MeV (approximately)

In comparing the binding energies of different nuclei, it is more useful to consider the binding energy per nucleon. For example, helium nucleus contains 4 nucleons (2 protons and neutrons), the binding energy per nucleon in this case is 28/4 = 7 MeV.

Binding energies of the nuclei of other atoms can be calculated in a similar manner. Figure 6.4 shows the binding thergies of the nuclei of atoms plotted against their respective Mass number. Three features of interest may be noted in this figure. First, nuclei with mass number around 60 have the highest binding energy per nucleon. Second, species of mass numbers 4, 12, and 16 have the nuclei lo have high binding energy per nucleon implying that the nuclei He⁴, Cl², and O¹⁶ are particularly stable. Third, the binding energy per nucleon decreases appreciably above mass number 100.

The form of relationship between binding energy per nucleon and mass number indicates that heavy nuclei would release mass and therefore energy) on division (or fission) into two nuclei of medium mass and that the light nuclei would release mass (and mass and that the light nuclei would receive therefore energy) on fusion to form heavier nuclei. These processes called fission and fusion are described later in chapter.



A plot of nuclear binding energy per nucleon against the mass Fig. 6.4 number for naturally occurring nuclides

ILLUSTRATION 6.28

What may be the new neutron and proton ratio after a nuclide ₀₂U²³⁸ loses an α-particle?

Sol. If the original neutron-proton ratio was n/Z (146/92), the new ratio will be (n-2)/(Z-2), i.e., 144/90.

ILLUSTRATION 6.29

The atomic mass of F19 is 18.9984 m_u. If the masses of proton and neutron are $1.0078\,\mathrm{m_n}$ and $1.0087\,\mathrm{m_n}$, respectively, calculate the binding energy per nucleon (ignore the mass of electrons). $(1 \text{ m}_{11} = 931 \text{ MeV})$

Sol. Mass defect

= [{(9 × 1.0078) + (10 × 1.0087)} - 18.9984]
$$m_{\tilde{u}}$$

$$= 0.1588 \text{ m}_{\text{u}}$$

Binding energy per nucleon

$$= (0.1588 \times 931) \text{ MeV}/19 = 7.78 \text{ MeV}$$

ILLUSTRATION 6.30

Which of the following causes the emission of X-rays?

- a. Electron capture
- **b.** γ-emission
- c. a-emission
- d. β-emission

Sol.

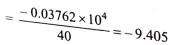
a. In certain nuclides, the nucleus captures an electron from the K-shell (being nearest to the nucleus). The vacancy created is filled up with the electron from the higher shells thereby emitting X-rays.

ILLUSTRATION 6.31

Calculate the packing fraction of Ar⁴⁰ (isotopic weight of Ar

Sol. Isotopic atomic weight of $Ar^{40} = 39.96238$ Mass number of $Ar^{40} = 40.00$

$$\therefore \text{ Packing fraction} = \frac{39.96238 - 40}{40} \times 10^4$$





 60m Co \longrightarrow 60 Co emits γ -radiations of wavelength 3 \times 10⁻¹⁰ m. Assuming each nuclei emits one wavelength, with what mass per mole of two nuclei differ?

a.
$$4.43 \times 10^{-9}$$
 g

b.
$$4.43 \times 10^{-6}$$
 g

c.
$$4.43 \times 10^{-3}$$
 g

Sol. E/Photon =
$$\frac{N \cdot hc}{\lambda}$$
; also $E = mc^2$

$$\therefore \frac{N \cdot hc}{\lambda}, = mc^2$$

or
$$m = \frac{Nh}{c\lambda} = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34}}{3 \times 10^8 \times 3 \times 10^{-10}}$$

= $4.43 \times 10^{-9} \text{ kg} = 4.43 \times 10^{-6} \text{ g}$

ILLUSTRATION 6.33

To which radioactive families do the following nuclides belong?

Sol. 222 Rn belongs to (4n + 2) family, i.e., uranium family.

 228 Ra belongs to (4n) family, i.e., thorium family.

²⁰⁷Pb belongs to (4n + 3) family, i.e., actinium family.

²⁰⁹Bi belongs to (4n + 1) family, i.e., neptunium family.

²³³Pa belongs to (4n + 1) family, i.e., neptunium family.

ILLUSTRATION 6.34

To which group of the periodic table does the last member of the following series belong?

- a. ₉₄Pu²³⁹ belongs to actinide series, hence it is present in third group.
- b. ₅₈Ce¹⁴⁰ belongs to lanthanide series, hence it is present in third group.
- c. ₈₄Po²¹⁸ belongs to VI group.

ILLUSTRATION 6.35

Calculate the neutron-proton ratio for each of the following radioactive nuclides.

a.
$$_{6}C^{14}$$
 b. $_{82}U^{238}$ **c.** $_{82}U^{212}$

a.
$$p = 6$$
, $n = 14 - 6 = 8$

$$\therefore \frac{n}{p} = \frac{8}{6} = 1.33$$

b.
$$p = 82$$
, $n = 238 - 82 = 146$

$$\frac{n}{p} = \frac{146}{92} = 1.54$$

c.
$$p = 82$$
, $n = 212 - 82 = 130$

$$\frac{n}{p} = \frac{130}{82} = 1.58$$

ILLUSTRATION 6.36

Show that a mass of 1.00 amu is equivalent to 931.5 MeV

Sol.
$$E = mc^2$$
, where $m = \text{mass defect}$

$$c = \text{velocity of light} = 3 \times 10^{10} \text{ cm s}^{-1}$$

$$\therefore E = 1.66 \times 10^{-24} \times (3 \times 10^{10})^2$$

$$= 14.94 \times 10^{-4} \text{ erg} = 1.494 \times 10^{-10} \text{ J}$$

$$(1 \text{ MeV} = 1.602 \times 10^{-13} \text{ J})$$

$$\therefore E = \frac{1.494 \times 10^{-10}}{1.602 \times 10^{-13}} = 931.5 \text{ MeV}$$

ILLUSTRATION 6.37

Calculate the mass defect and binding energy per nucleon for an alpha particle (containing two protons and two neutrons) whose actual mass is 4.0028 amu (mass of proton = 1.00759 amu, mass of neutron = 1.00898 amu).

Sol.

Expected mass of an α-particle

$$= 2 \times 1.00759 + 2 \times 1.00898$$

$$= 4.03314$$
 amu

Actual mass = 4.0028 amu

Mass defect = 4.03314 - 4.0028

= 0.03034 amu

Binding energy = $0.03034 \times 931 \text{ MeV}$

= 28.2465 MeV

Binding energy per nucleon

$$= \frac{28.2465}{4} = 7.062 \text{ MeV}$$

ILLUSTRATION 6.38

Which of the following are radioactive?

b.
$$_{49}In^{114}$$

Sol.

b. 49 In 144. It has an odd number of proton and odd number of neutrons.

$$p = 49$$
, $n = 114 - 49 = 65$

ILLUSTRATION 6.39

Which of the following is least stable?

b.
$$_{13}Al^{30}$$
 c. $_{50}Sn^{119}$

b. 13A130, odd number of protons and odd number of neutrons.

$$p = 13$$
, $n = 30 - 13 = 17$.

which of the following nuclides are β^{\odot} and β^{\oplus} emitter, and stable nuclides?

$$\frac{1}{a \cdot 20} Ca^{49}$$
 b. $\frac{1}{80} Hg^{195}$ **c.** $\frac{1}{82} Pb^{208}$

$$a._{20}Ca^{45}$$
 $b._{80}^{12}$ $c._{82}^{12}$ $e._{67}Ho^{150}$ $f._{13}Al^{30}$ $g._{50}Sn^{120}$

$$f_{-13}Al^{30}$$

 β^{\odot} -emitter \Rightarrow **a.** $_{20}$ Ca⁴⁹ **f.** $_{13}$ Al³⁰ **h.** $_{36}$ Kr⁹⁴ All of them have Z less than 82.

a.
$$_{20}\text{Ca}^{49} \Rightarrow \frac{n}{p} = \frac{29}{20} = 1.45$$
 | h/p is higher lowered by β^{\odot} -emission

n/p is higher and is (atomic weight < 82).

f.
$$_{13}\text{Al}^{30} \Rightarrow \frac{n}{p} = \frac{17}{13} = 1.3$$

[Same reason]

h.
$$_{36}\text{Kr}^{94} \Rightarrow \frac{n}{p} = \frac{58}{36} = 1.3$$

[Same reason]

$$\beta^{\oplus}$$
-emitter \Rightarrow **b.** $_{80}Hg^{195}$

d.
$$_{5}B^{8}$$

All of them are Z less than 82.

b.
$$_{80}$$
Hg¹⁹⁵, $\frac{n}{p} = \frac{115}{80} = 1.43$. n/p is lower than the stability belt for Hg, n/p should be equal

n/p is lower than the to 1.53.

n/p is lower than 1.53, so it will emit β^{\oplus} to increase n/p ratio.

d.
$$_{5}B^{8}$$
, $\frac{n}{n} = \frac{3}{5} = 0.6$,

(for stability n/p ratio = 1).

n/p is lower than 1. $\left(Z \text{ up to } 20, \frac{n}{p} = 1\right)$. It is β^{\oplus} emitter.

e.
$$_{67}\text{Ho}^{150}$$
, $\frac{n}{n} = \frac{33}{67} = 1.2$.

e. ₆₇Ho¹⁵⁰, $\frac{n}{p} = \frac{33}{67} = 1.2$. (For stability with Z > 60, n/p should be 1.50.

n/p is lower than 1.5. So β^{\oplus} emitter.

Stable nuclides

$$_{92}$$
Pb²⁰⁸, $_{50}$ Sn¹²⁰

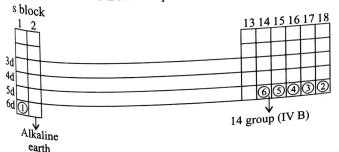
Both have even number p and even number of n. These are stable nuclides.

ILLUSTRATION 6.41

An alkaline earth metal is radioactive. It and its daughter element decay by emitting 3 α -particles in succession. In what group should the resulting element be formed?

Sol. $3\alpha \Rightarrow 3$ He⁴ \Rightarrow Atomic number decreases by 6.

 \Rightarrow Loss of 6 p and 6 n.



The resulting element will be in 14th group.

ILLUSTRATION 6.42

If a nuclide of an element in group I A (Ist group) undergoes radioactive decay be emitting β^{\oplus} , what will be the periodic group of the resulting element?

Sol. β^{\oplus} -emitter $\binom{1}{1}e^0$, the atomic number decreases by 1.

$$_{a}X^{b}\longrightarrow _{a-1}Y^{b}+_{+1}e^{0}$$

Resulting element will be a noble gas (group 18).

ILLUSTRATION 6.43

Which is more unstable of each of the following pairs, and in each case what type of process could the unstable nucleus undergo?

a.
$$_{6}C^{16}$$
, $_{7}N^{16}$

Sol.

a. In this case although ${}_{6}C^{16}$ has even number of p and n, still its n/p ratio is higher than n/p ratio of $_7N^{16}$,

$$\frac{n}{p} \text{ of } {}_6\mathrm{C}^{16} = \frac{10}{6} = 1.7$$
 For $Z = 20, n/p$ should be $= 1$. For stability

For
$$Z = 20$$
, n/p should be = 1.
For stability

n/p ratio is higher than 1. It would emit β^{\odot} to get n/p ratio back to stable range.

$$_{6}C^{16} \longrightarrow _{7}N^{14} + _{-1}e^{0}$$

$$\frac{n}{p} = \frac{10}{6} = 1.7, \ \frac{n}{p} = \frac{7}{7} = 1$$

In case of
$$_{7}N^{16}$$
, $\frac{n}{p} = \frac{9}{7} = 1.2$

n/p of ${}_{6}C^{16} > n/p$ of ${}_{7}N^{16}$. So ${}_{6}C^{16}$ more unstable than

b. In this case although ${}_{0}F^{18}$ has odd number p and n, still its n/p ratio is equal 1, has n/p of $_{10}$ Ne¹⁸ is less than 1.

$$\frac{n}{n}$$
 of $_{9}F^{18} = \frac{9}{9} = 1$

$$\frac{n}{p}$$
 of $_{9}F^{18} = \frac{9}{9} = 1$ (For Z = 20, stability $n/p = 1$)

$$\frac{n}{n}$$
 of $_{10}$ Ne¹⁸ = $\frac{8}{10}$ = 0.8 (Its value is less than 1)

So 10 Ne 18 would be unstable than oF 18.

So, it will emitt β^{\oplus} or K-capture to get the ratio into the range of stability.

$$_{10}$$
Ne¹⁸ $\longrightarrow _{9}$ F¹⁸ + $_{+1}$ e⁰

$$\frac{n}{p} = \frac{8}{10} = 0.8 \text{ or } \frac{n}{p} = \frac{9}{9} = 1 \ (0.8 \longrightarrow 1)$$

$$_{10} \text{Ne}^{18} + _{+1} e^0 \longrightarrow {}_{0} \text{F}^{18}$$

ILLUSTRATION 6.44

To what stable isotope 103Lr²⁵⁷ decay?

 $_{103}$ Lr²⁵⁷ is a member of (4n + 1) series and would decay

Which one of the following processes α , β^{\ominus} , β^{\oplus} , or K-capture cause

- An increase in atomic number
- A decrease in atomic number b.
- Emission of X-ray

Sol. a. β⊖

b. α , β^{\oplus} , and K-capture **c.** K-caputre.

ILLUSTRATION 6.46

Out of the four series, which series disintegrates in a least branching manner?

Sol. (4n + 1) has least branching (artificial series). In 4n, (4n + 2), and (4n + 3) (natural series), there are certain elements which disintegrate in a braching process by emitting α - or β -particles. The species thus formed are then disintegrated in such a way as to give a common product.

ILLUSTRATION 6.47

In radioactive series, an inner transition element 92 U238 loses one α-particle and one β-particle to produce a very unstable daughter nuclei or Pa²³⁴ with half life 1.14 min. Find out the displacement in group due to these emissions.

Sol. The reaction is:

$$_{92}U^{238} \xrightarrow{-\alpha} _{90}Th^{234} \xrightarrow{-\beta} _{91}Pa^{234}$$

Since elements from 89Ac to 103Lw exist is the same group, where as from 90 Th to 103 Lw are inner transition elements of actinium series, so group will not change. In this case, group displacement law is not valid. The daughter element will be in same group III B.

ILLUSTRATION 6.48

Predict by what mole(s) spontaneous radioactive decay will proceed for each of the following unstable isotopes:

a. $_2$ He⁶ **b.** $_9$ F¹⁸ **c.** $_{93}$ Np⁴¹ **d.** $_{91}$ Pa²³⁵

Sol.

a.
$$_{2}\text{He}^{6}$$
; $p = 2$; $n = 4 \Rightarrow \frac{n}{p} = \frac{4}{2} = 2(\text{high})$
 $\therefore \beta\text{-decay}$

b.
$$_{9}F^{18}$$
; $p = 9$; $n = 9 \Rightarrow \frac{n}{p} = \frac{9}{9} = 1$

c.
$$_{93}\text{Np}^{241}$$
; $p = 93$; $n = 148 \Rightarrow \frac{n}{p} = \frac{148}{93} = 1.6$ (high)

and $Z > 82 \Rightarrow \alpha$ or β decay

d.
$$_{91}\text{Po}^{235}$$
; $p = 91$; $n = 144 \Rightarrow \frac{n}{p} = \frac{144}{91} = 1.58 \text{ (high)}$
and $Z > 82 \Rightarrow \alpha$ - or β -decay

CONCEPT APPLICATION EXERCISE 6.2

- 1. In the reaction ${}_{1}H^{2} + {}_{1}H^{3} \longrightarrow {}_{2}He^{4} + {}_{0}n^{1}$. If the binding energies of $_{1}H^{2}$, $_{1}H^{3}$, and $_{2}He^{4}$ are, respectively, a, b, and c(in MeV), then calculate the energy released in this reaction.
- 2. Calculate the mass loss in the following reaction:

$$_{1}H^{2} + _{1}H^{3} \longrightarrow _{2}He^{4} + _{0}n^{1}$$

Given masses: $_{1}H^{2} = 2.014$ amu; $_{1}H^{3} = 3.016$ amu $_{2}$ He⁴ = 4.004 amu; $_{0}$ n¹ = 1.008 amu

3. Calculate the energy change during the reaction $_{3}\text{Li}^{7} + _{1}\text{H}^{1} \longrightarrow 2_{2}\text{He}^{4}$

Given $\Delta m = 0.0185$ amu.

4. How much energy will be released during the following reaction?

$$_{6}C^{14} \longrightarrow {}_{7}H^{14} + {}_{-1}e^{0}$$

Atomic masses of C^{14} and N^{14} are 14.00324 and 14.00307 amu, respectively.

ANSWERS

1. c - a - b

2. 0.018 amu 3. 17.2235 MeV

4. 0.15827 MeV

6.10 RATE OF RADIOACTIVE DISINTEGRATION

The decay of a radioactive element is a random process and is independent of external factors such as temperature, pressure, and environmental changes. The radioactive disintegration follows first-order kinetics and hence the expression for the rate constant can be derived as follows:

Suppose a radioactive element A disintegrates to form an element B, i.e.,

$$A \longrightarrow B$$

Let N_0 = total number of atoms present originally in the sample

N = total number of atoms left in the sample at time t

dN = a small number of atoms that disintegrate in a small interval of time dt

Therefore, rate of disintegration of the element = $-\frac{cN}{3t}$

(minus sign indicated that the number of atoms left undecayed decreases with time)

According to the radioactive decay law,

$$-\frac{\partial N}{\partial t} \propto N \qquad ...(i)$$

$$-\frac{\partial N}{\partial t} = KN \qquad ...(ii)$$

where K is constant, characteristic of the nature of the radioactive element and is called decay or disintegration constant.

The rate of disintegration is also called the activity. Hence, activity = KN. It is measured by counting the number of particles per unit time using instruments such as scintillation counter, Geiger counter, and Wilson cloud chamber per uniter, and Wilson cloud chamber.

Multiplies symbol λ is quite often used in place of K.

Equation (ii) can be rewritten as

$$-\frac{dN}{N} = Kdt \qquad ...(iii)$$

putting dt = 1 s, we get

$$K = -\frac{dN}{N} \qquad ...(iv)$$

Hence the disintegration constant may be defined as the faction of the total number of atoms, which disintegrate in one second at any instant of time.

$$-\ln N = Kt + C \qquad \dots (v)$$

where C is a constant of integration.

But when t = 0, $N = N_0$ (as already stated)

$$-\ln N_0 = 0 + C$$

Putting this value in Eq. (v), we get

$$-\ln N = Kt - \ln N_0$$

or
$$Kt = \ln N_0 - \ln N = \ln \frac{N_0}{N} = 2.303 \log \frac{N_0}{N}$$
 ...(vii)

or
$$K = \frac{2.303}{t} \log \frac{N_0}{N} \qquad \dots \text{(viii)}$$

This equation is also sometimes written as

$$K = \frac{2.303}{t} \log \frac{a}{a - x}$$

where a is the amount of the radioactive substance initially taken and a-x is the amount present at time t. Evidently, the units of K will be time-1 such as second-1, hour-1, year-1, etc.

Equation (vii) can also be written in the exponential form as

$$\frac{N_0}{N} = e^{Kt} \quad \text{or} \quad \frac{N}{N_0} = e^{-Kt}$$

$$V = N_0 e^{-Kt} \qquad \dots \text{(ix)}$$

Equation (ix) shows that the radioactive decay is exponential 45 shown in Fig. 6.5. The figure shows that N = 0 only at $t = \infty$.

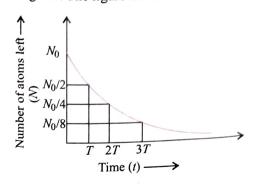


Fig. 6.5

6.10.1 HALF-LIFE PERIOD

Half life of a radioactive element is defined as the time during which half the number of atoms present initially in the sample of the element decay.

It is a characteristic constant of a radioactive isotope and varies from millions of years to fraction of second depending only upon the nature of isotope (e.g., 4.5×10^9 years for $_{92}U^{238}$ and 10^{-4} s for ₈₄Po²¹⁴).

Putting $t = t_{1/2}$ when $N = N_0/2$ in Eq. (viii), we get

$$t_{1/2} = \frac{2.303}{K} \log \frac{N_0}{N_0/2} = \frac{2.303}{K} \log 2 = \frac{2.303}{K} \times 0.3010$$

or
$$t_{1/2} = \frac{0.693}{K}$$

From this equation, we observe that the half-life period $(t_{1/2})$ is independent of the initial amount. In fact, it is for this reason that it is preferred to express the life of a radioactive element in terms of half-life period. For example, the half-life period of radium is 1620 years. This means that 100 g of radium will be reduced to 50 g in 1620 years which will be further reduced to 25 g in a further 1620 years and so on.

Expression for the calculation of the amount of radioactive substance left after n half lives

Let the initial amount of a radioactive substance be N_0 .

After one half-life period $(t_{1/2})$, it becomes = $N_0/2$

After two half-life periods $(2t_{1/2})$, it becomes = $N_0/4$

After three half-life periods $(3t_{1/2})$, it becomes = $N_0/8$

After *n* half-life periods $(nt_{1/2})$, it shall become = $\left(\frac{1}{2}\right)^n N_0$

Thus, for the total disintegration of a radioactive substance an infinite time will be required.

	me T)	Amount of radioactive substance (N)	Amount of radioactive substance decomposed $(N_0 - N)$
()	N_0	0
t ₁	/2	$\frac{1}{2}N_0 = \left(\frac{1}{2}\right)^1 N_0$	$\frac{1}{2} N_0 = \left[1 - \frac{1}{2} \right] N_0$
2t	1/2	$\frac{1}{4}N_0 = \left(\frac{1}{2}\right)^2 N_0$	$\frac{3}{4}N_0 = \left[1 - \frac{1}{4}\right]N_0$
3t ₁	1/2	$\frac{1}{8}N_0 = \left(\frac{1}{2}\right)^3 N_0$	$\frac{7}{8} N_0 = \left[1 - \frac{1}{8} \right] N_0$
4t1	/2	$\frac{1}{16} N_0 = \left(\frac{1}{2}\right)^4 N_0$	$\frac{15}{16} N_0 = \left[1 - \frac{1}{16} \right] N_0$
nt ₁	/2	$\left(\frac{1}{2}\right)^n N_0$	$\left[1-\left(\frac{1}{2}\right)^n\right]N_0$

Amount of radioactive substance left after n half-life periods $N = \left(\frac{1}{2}\right)^n N_0$

and total time $T = n \times t_{1/2}$, where n is a whole number.

6.10.2 AVERAGE LIFE

Evidently, the whole of the radioactive element can never disintegrate or, in other words, the time required for the disintegration of the whole of a radioactive element will be infinity.

Thus, it is meaningless to talk of the total life of a radioactive element. However, sometimes another term is used, called average life (τ) which is the reciprocal of the disintegration constant (K), i.e.,

Average life (
$$\lambda$$
) = $\frac{1}{K} = \frac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}$

or Average life =
$$\frac{\text{Total life time of all the atoms}}{\text{Total number of atoms}}$$

The average life of a radioactive substance is 1.44 times of its half-life period.

Alternatively,

We know that
$$K = \frac{2.303}{t} \log \left(\frac{N_0}{N} \right)$$

or $Kt = 2.303 \log \left(\frac{N_0}{N} \right) = \ln \left(\frac{N_0}{N} \right)$ [ln = 2.303 log]

$$\therefore e^{Kt} = \frac{N_0}{N}$$

or
$$\frac{N}{N_0} = e^{-Kt}$$

Let
$$\tau = \frac{1}{K}$$
, then $\frac{N}{N_0} = e^{-1} = \frac{1}{e}$
 $\frac{N}{N_0} = \frac{1}{2.718} = 0.3679$ $(e = 2.718)$

% remaining amount
$$\frac{N}{N_0} \times 100 = 0.3679 \times 100 = 36.79$$

% decayed amount = 100 - 36.79 = 63.21

Time during which 63.21% substance undergoes decay is called average life.

Relation between rate of decay and mass of given element

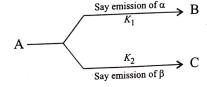
Rate
$$\left(-\frac{\partial N}{\partial t}\right) = K \times N$$

 $= K \times \text{Number of atoms of element}$
 $= \frac{0.693}{t_{1/2}} \times \frac{\text{Mass}}{\text{Atomic mass}}$
 $\times \text{Avogadro's number}$

$$K = \frac{0.693}{t_{\text{tra}}}$$

Parallel radioactive disintegration

A radioactive element A decays to B and C in two parallel paths as:



The average decay constant for element A can be expressed as $K = K_1 + K_2.$

The fractional yield of B =
$$\frac{K_1}{K_1 + K_2}$$

The fractional yield of C =
$$\frac{K_2}{K_1 + K_2}$$

For example,

Say emission of
$$\alpha$$

$$R_{1} \longrightarrow R_{7}Fr^{223} + {}_{2}He^{4}$$

$$R_{2} \longrightarrow R_{2}Fr^{223} + {}_{2}He^{4}$$
Say emission of β

$$R_{2} \longrightarrow R_{2}Fr^{223} + {}_{2}He^{4}$$

$$R_{3}Fr^{223} + {}_{2}He^{4}$$
Overall everage disintegration constant = $K_{1} + K_{2}$

Overall average disintegration constant = $K_1 + K_2$

Fractional yield of Fr =
$$\frac{K_1}{K_1 + K_2}$$

Fractional yield of Th =
$$\frac{K_2}{K_1 + K_2}$$

Maximum yield of daughter element

A radioactive element A decays to give a daughter element B which further decays to another daughter element C and so on till a stable element is formed (A \rightarrow B \rightarrow C). Also if the number of daughter atoms at t = 0 is zero and parent atom is much more lived than daughter (i.e., $K_A < K_B$), where K_A and K_B are decay constants of A and B, respectively, then the number of atoms of daughter element B after time t is

$$N_{\rm B} = \frac{N_0 K_{\rm A}}{K_{\rm B} - K_{\rm A}} [e^{-K_{\rm A}t} - e^{-K_{\rm B}t}]$$

Maximum activity of daughter element can be expressed at

$$t_{\text{max}} = \frac{2.303}{K_{\text{B}} - K_{\text{A}}} \log \left[\frac{K_{\text{B}}}{K_{\text{A}}} \right]$$

Relationship between half-life time and time for x% decay

We know
$$t_{1/2} = \frac{0.69}{K} = \frac{0.3 \times 2.3}{K}$$
 ...(i)

and decay constant
$$K = \frac{2.3}{t_x} \log \frac{a}{a - x}$$
 ...(i

where t_x is the time required to decay to x%, a = initial amount, and a - x = amount left after time t_x .

Dividing Eq. (i) by Eq. (ii), we get

$$\frac{t_x}{t_y} = \frac{\log\left(\frac{a}{a-x}\right)}{\log\left(\frac{a}{a-y}\right)}$$

This can be used directly to calculate time required for $x^{\%}$ decay.

Similarly, for two different amounts of decay, let say x and y, we have

$$\frac{N_1}{N_2} = \frac{\log\left(\frac{a}{a-x}\right)}{\log\left(\frac{a}{a-y}\right)}$$

Units of radioactivity In the State of radioactivity is becquered (Bq) named after Antonine which is equal to one disintegration and the state of named after Anguerel which is equal to one disintegration per second.

 $\frac{1}{1}$ Becquerel (1 Bq) = 1 disintegration per second

Rutherford (1 Rd) = 10⁶ disintegration per second.

The older unit, curie, named after Marie Curie is still used; curie (Ci) is defined as the amount of radioactive isotope that one curre (3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second (the activity associated gives 3.7 × 10¹⁰ disintegrations per second gives 3.7 × 10¹⁰ disintegrations per second gives 3.7 × 10¹⁰ disintegrations per second gives 3.7 × 10¹⁰ disintegration gives 3.7 × 10¹ gives 3.7 care activity associated gives 3.7 radium-225 with half-life of 1600 years). Thus, 1 Ci = $\frac{1000 \text{ Hz}}{1000 \text{ Hz}}$ disintegrations s⁻¹ = 3.7 × 1010 B. $^{\text{n/II}_{15}}_{3,7} \times 10^{10} \text{ disintegrations s}^{-1} = 3.7 \times 10^{10} \text{ Bq}.$

6.11 RADIOACTIVE EQUILIBRIUM

Let us consider that a radioactive element A disintegrates to give gwhich is also radioactive and disintegrates into C.

$$A \longrightarrow B \longrightarrow C$$

The element B is said to be in radioactive equilibrium with Aif its rate of formation from A is equal to its rate of decay into C_{1} If K_{1} and K_{2} are the disintegration constants of A and B, N_{1} and N_2 the number of atoms of each radioactive element present at equilibrium, then we have

Rate of formation of B = Rate of decay of A = K_1N_1

Rate of decay of B = K_2N_2

At radioactive equilibrium,

$$K_1 N_1 = K_2 N_2$$

or
$$\frac{N_1}{N_2} = \frac{K_2}{K_1} = \frac{\frac{1}{K_1}}{\frac{1}{K_2}} = \frac{\text{Average life of A}}{\text{Average life of B}}$$

Thus, the number of atoms of A and B are in the ratio of their average life periods.

$$\frac{N_1}{N_2} = \frac{(t_{1/2})_2}{(t_{1/2})_1}$$

When K_A of parent element is less than K_B of daughter element, but both are not very small, then a transient equilibriums reached, when

$$\frac{N_{\rm B}}{N_{\rm A}} = \frac{K_{\rm A}}{K_{\rm B} - K_{\rm A}}$$

In fact it is steady state.

ILLUSTRATION 6.49

Calculate $t_{1/2}$ for Am²⁴¹ in years given that it emits 1.2×10^{11} . Q-particles per gram per second.

Sol. 1 gram of Am contains $N_A/241$ nuclei = N_0 .

Using the equation,

Rate of decay =
$$1.2 \times 10^{11} \text{ s}^{-1}$$

= $K \times N_0$
= $K \times N_A/241$
= $K \times 6.02 \times 10^{23}/241$

$$K = 1.2 \times 10^{11} \times 241/6.02 \times 10^{23}$$

= 4.8×10^{-11} s⁻¹
and $t_{1/2} = \ln 2/K = 0.693/K$
= $(0.693)/4.8 \times 10^{-11}$
= 1.40×10^{10} s = 458 years

ILLUSTRATION 6.50

How many atoms of 0.1 g-atom of a radioactive isotope zXA (half life = 5 days) will decay during the 11th day?

Sol. Amount of radioactive substance = 0.1 g-atom

So
$$N_0 = 0.1 \times \text{Avogadro's number}$$

= $0.1 \times 6.02 \times 10^{23}$
= $6.02 \times 10^{22} \text{ atoms}$

Number of atoms after 5 days =
$$\frac{6.02 \times 10^{22}}{2}$$
 = 3.01×10²²

Number of atoms after 10 days =
$$\frac{3.01 \times 10^{22}}{2}$$

= 1.505 × 10²

Let the number of atoms left after 11 days be N.

We know that

$$t = \frac{2.303}{K} \log \frac{N_0}{N}$$

Given
$$t = 11$$
, $K = \frac{0.693}{5}$, $N_0 = 6.02 \times 10^{22}$

So,
$$11 = \frac{2.303 \times 5}{0.693} \log \frac{6.02 \times 10^{22}}{N}$$

or log
$$\frac{6.02 \times 10^{22}}{N} = \frac{11 \times 0.693}{2.303 \times 5} = 0.6620$$

$$\frac{6.02 \times 10^{22}}{N} = \text{Antilog } 0.6620 = 4.592$$

So,
$$N = \frac{6.02}{4.592} \times 10^{22} = 1.3109 \times 10^{22}$$
 atoms decayed during 11th day.

ILLUSTRATION 6.51

10 g-atoms of an α-active radioisotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm³. Calculate the half life of the radioisotope.

Sol. Amount of radioactive isotope = 10 g-atoms

$$N_0 = 10 \times 6.023 \times 10^{23}$$
 atoms
= 6.023×10^{24} atoms

22400 cm³ of helium will contain = 6.023×10^{23} atoms

11.2 cm³ helium will contain =
$$\frac{6.023 \times 10^{23}}{22400} \times 11.2 \text{ atoms}$$

$$= 3.01 \times 10^{20}$$
 atoms

As one helium atoms is obtained by disintegration of one atom of radioisotope, the total number of atoms of the radioactive isotope which have disintegrated in one hour

$$= 3.01 \times 10^{20}$$
 or 0.0003×10^{24}

The number of atoms of radioactive isotope left after one hour,

$$N = 6.023 \times 10^{24} - 0.000301 \times 10^{24}$$

$$= 6.0227 \times 10^{24}$$
Using, $K = \frac{2.303}{t} \log \frac{N_0}{N}$

$$= \frac{2.303}{t} \log \frac{6.023 \times 10^{24}}{6.0227 \times 10^{24}}$$

$$= 2.303 \times 2.1632 \times 10^{-5} = 4.982 \times 10^{-5} \text{ hr}^{-1}$$

$$t_{1/2} = \frac{0.693}{(4.982 \times 10^{-5} \times 24 \times 365)} = 1.58 \text{ years}$$

ILLUSTRATION 6.52

The half-life period of radon is 3.8 days. After how many days will only one-twentieth of radon sample be left over?

Sol. We know that
$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.8} = 0.182 \text{ day}^{-1}$$

Let the initial amount of radon be N_0 and the amount left after t days be N which is equal to $N_0/10$.

Applying the equation,

$$t = \frac{2.303}{K} \log \frac{N_0}{N}$$

$$t = \frac{2.303}{0.182} \log \frac{N_0}{N_0/10}$$

$$= \frac{2.303}{0.182} \log 10 = 12.65 \text{ days}$$

Alternatively

$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log \frac{a}{a - x}}$$

$$\Rightarrow \frac{3.8}{t_{x\%}} = \frac{0.3}{\log \frac{a}{\frac{1}{10}a}} \quad \text{or} \quad \frac{3.8}{t_{x\%}} = \frac{0.3}{\log 10}$$

$$\therefore t_{x\%} = \frac{3.80}{0.3} = 12.65 \text{ days}$$

ILLUSTRATION 6.53

A counter rate metre is used to measure the activity of a radioactive sample. At a certain instant, the count rate was recorded as 400 counters per minute. Five minutes later, the count rate recorded was 200 counts per min. Calculate the decay constant and half-life period of the sample.

Sol. Let N_0 and N be the number of atoms of the radioactive substance present at the start and after 5 min, respectively. Rate of disintegration at the start = $KN_0 = 400$ and rate of disintegration after 5 min = KN = 200

Dividing both,
$$\frac{KN_0}{KN} = \frac{400}{200}$$

or
$$\frac{N_0}{N} = 2.00$$

We know that
$$K = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$K = \frac{2.303}{5} \log 2.00 = 0.138 \,\mathrm{min^{-1}}$$

Half-life period =
$$\frac{0.693}{K} = \frac{0.693}{0.138} = 5.0 \text{ min}$$

ILLUSTRATION 6.54

1 g of $_{79}$ Au¹⁹⁸ ($t_{1/2}$ = 65 hr) decays by β -emission to produce stable Hg.

- a. Write nuclear reaction for process.
- b. How much Hg will be present after 260 hr.

Sol.

a.
$$_{79}$$
Au¹⁹⁸ \longrightarrow $_{80}$ Hg¹⁹⁸ + $_{-1}e^0$

b.
$$t_{1/2} = 65 \text{ hr}$$

$$T = 260 \text{ hr}$$

$$T = t_{1/2} \times n$$

$$\therefore \text{ Number of halves } (n) = \frac{260}{65} = 4$$

Now, amount left undecayed (N) = $\frac{N_0}{2^4} = \frac{1}{2^4} = \frac{1}{16}$ g

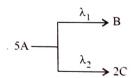
∴ Amount of Au decayed =
$$\frac{15}{16}$$
 g

· 198 g Au gives 198 g Hg.

$$\therefore \frac{15}{16} g \text{ Au gives } \frac{15}{16} g \text{ Hg.}$$

ILLUSTRATION 6.55

A follows parallel path of first-order reactions giving B and C as:



If the initial concentration of A is 0.25 M, calculate the concentration of C after 5 hr of reaction.

Given,
$$\lambda_1 = 1.5 \times 10^{-5} \text{ s}^{-1}$$
, $\lambda_2 = 5 \times 10^{-6} \text{ s}^{-1}$

Sol.
$$\lambda_A = \lambda_1 + \lambda_2 = 1.5 \times 10^{-5} + 5 \times 10^{-6} = 20 \times 10^{-6} \text{ s}^{-1}$$

Also, 2.303
$$\log \frac{[A]_0}{[A]_t} = \lambda \times t$$

$$\therefore 2.303 \log \frac{0.25}{[A]_t} = 20 \times 10^{-6} \times 5 \times 60 \times 60$$

$$\therefore [A]_{t} = 0.1744 \text{ M}$$

$$[A]_{decomposed} = [A]_0 - [A]_t = 0.25 - 0.1744$$

$$= 0.0756 \text{ M}$$

$$= \left[\frac{\lambda_2}{\lambda_1 + \lambda_2}\right] \times [A]_{decomposed} \times \frac{2}{5}$$

$$= 0.0756 \times \frac{5 \times 10^{-6}}{20 \times 10^{-6}} \times \frac{2}{5}$$

$$= 7.56 \times 10^{-3} \text{ M}$$

ILLUSTRATION 6.56

The activity of the hair of an Egyptian mummy is 7 disintegration $\frac{1}{100}$ of C¹⁴. Find the age of mummy. Given $t_{0.5}$ of C¹⁴ is 5770 year and disintegration rate of fresh sample of C¹⁴ is 14 disintegration min-1.

Sol.
$$r_0 = 14 \text{ dpm}, \quad r = 7 \text{ dpm}$$

$$\therefore \frac{r_0}{r} = 2$$

Also, rate at any time ∝ number of atoms

$$\frac{r_0}{r} = \frac{N_0}{N} = 2$$
Now, $t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N} = \frac{2.303 \times 5770}{0.693} \log_{10} 2$

t = 5770 year.

LLUSTRATION 6.57

Half life of a radioactive sample is 2x years. What fraction of this sample will remain undecayed after x years?

a.
$$\frac{1}{2}$$

$$\frac{1}{\sqrt{2}}$$

a.
$$\frac{1}{2}$$
 b. $\frac{1}{\sqrt{2}}$ **c.** $\frac{1}{\sqrt{3}}$

b.
$$K = \frac{2.303}{t} \log\left(\frac{N_0}{N}\right)$$
$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log\left(\frac{N_0}{N}\right)$$
$$\frac{0.693}{2x} = \frac{2.303}{x} \log\left(\frac{N_0}{N}\right)$$
$$\frac{1}{2} \log 2 = \log\left(\frac{N_0}{N}\right)$$
$$\frac{N}{N_0} = \frac{1}{\sqrt{2}}$$
Fraction undecayed =
$$\frac{1}{\sqrt{2}}$$

ILLUSTRATION 6.58

Which among the following relations is correct?

a.
$$t_{3/4} = 2t_{1/2}$$

b.
$$t_{3/4} = 3t_{1/2}$$

c.
$$t_{1/2} = 2t_{3/4}$$

d.
$$t_{1/2} = 3t_{3/4}$$

Sol. a. We know that
$$K = \frac{2.303}{t} \log \left(\frac{N_0}{N} \right)$$

or
$$K = \frac{0.693}{t_{1/2}}$$

$$\therefore \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{100}{75}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{3/4}} \log 1.333$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{3/4}} \times 0.125$$
or $t_{3/4} = 2t_{1/2}$

ILLUSTRATION 6.59

The half-life period of radium is 1600 years. Calculate the disintegration of radium.

Sol. Given that half-life period $(t_{1/2}) = 1600$ years

We know that
$$K = \frac{0.693}{t_{1/2}}$$

$$\therefore K = \frac{0.693}{1600}$$

$$K = 4.33 \times 10^{-4} \text{ year}^{-1}$$

ILLUSTRATION 6.60

A radioactive element has half life of 4.5×10^9 years. If 80 g of this was taken, the time taken for it to decay to 40 g will be

a.
$$2.25 \times 10^9$$
 years

b.
$$4.50 \times 10^9$$
 years

c.
$$6.75 \times 10^9$$
 years **d.** 8.75×10^9 years

d.
$$8.75 \times 10^9$$
 year

Sol. b.
$$t_{1/2} = 4.5 \times 10^9$$
 years

Here the amount decay to 50%, i.e. from 80 g to 40 g. Therefore time required will be 4.5×10^9 years.

ILLUSTRATION 6.61

The half-life period of a radioactive element is 140 days. After 560 days, 1 g of the element will reduce to

Sol. d.
$$T = 560$$
 days, $t_{1/2} = 140$ days

$$\therefore n = \frac{T}{t_{1/2}} = \frac{560}{140} = 4$$

:.
$$N = \left(\frac{1}{2}\right)^n N_0 = \left(\frac{1}{2}\right)^4 \times 1 = \frac{1}{16} g$$

ILLUSTRATION 6.62

A radioactive isotope decays at such a rate that after 96 min, only 1/8th of the original amount remains. The value of $t_{1/2}$ of this nuclide is

- a. 12 min
- **b.** 32 min
- c. 24 min
- d. 48 min

Sol. b.
$$K = \frac{2.303}{t} \log \frac{a}{a - x}$$

or
$$\frac{0.693}{t_{1/2}} = \frac{2.303}{96} \log \frac{a}{\frac{a}{8}}$$

Second method

$$\frac{t_{1/2}}{t_{1/8}} = \frac{0.3}{\log \frac{a}{a/8}}$$

$$\therefore \frac{t_{1/2}}{96} = \frac{0.3}{\log 8}$$

$$\frac{t_{1/2}}{96} = \frac{0.3}{\log 2^3}$$

$$\therefore t_{1/2} = \frac{0.3 \times 96}{3 \times \log 2} = 32 \min$$

ILLUSTRATION 6.63

80% of the radioactive nuclei present in a sample is found to remain undecayed after one day. The percentage of undecayed nuclei left after two days will be

Sol. a.
$$K = \frac{2.303}{t} \log \left(\frac{N_0}{N} \right)$$

= $\frac{2.303}{1} \log \left(\frac{100}{80} \right) [t = 1 \text{ day}]$...(i)

$$K = \frac{2.303}{2} \log \left(\frac{100}{N} \right) [t = 2 \text{ day}]$$
 ...(ii)

$$\frac{2.303}{1}\log\left(\frac{100}{80}\right) = \frac{2.303}{2}\log\left(\frac{100}{N}\right)$$

$$\left(\frac{5}{4}\right)^2 = \frac{100}{N}$$

$$N = 64$$

ILLUSTRATION 6.64

A radioactive substance has a half life of 5 days. After 20 days it was found that 3 g of the isotope left in the container. The initial weight of the isotope was

Sol. a.
$$t_{1/2} = 5$$
 days, $T = 20$ days

We know
$$T = nt_{1/2}$$

$$\therefore n = \frac{T}{t_{1/2}} = \frac{20}{5} = 4$$

$$N = \left(\frac{1}{2}\right)^n N_0$$

$$N_0 = N \times (2)^4 = 3 \times (2)^4 = 48 \text{ g}$$

ILLUSTRATION 6.65

The half life of radium (226) is 1620 years. The time taken to convert 10 g of radium to 1.25 g is

b. 1620 years

c. 3240 years

d. 4860 years

Sol. d. $t_{1/2} = 1620$ years

$$N_0 = 10 \text{ g}$$

$$N = 1.25 \text{ g}$$

We know
$$K = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\Rightarrow \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{10}{1.25}$$

$$\therefore t = \frac{2.303 \times 1620}{0.693} \log \frac{10}{1.25} \approx 4860 \text{ years}$$

Alternatively

$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log \frac{a}{a - x}} = \frac{0.3}{\log \frac{10}{1.25}} = \frac{0.3}{\log 8} = \frac{0.3}{3 \times 0.3}$$

$$\therefore t_{x\%} = t_{1/2} \times 3 = 1620 \times 3 = 4860 \text{ years}$$

ILLUSTRATION 6.66

If equal number of atoms of two radioactive elements are considered, the most dangerous would be the one with a half

- a. 4.0 million years
- **b.** 100 years
- c. 0.01 second
- d. 1 second

Sol. c. Lesser the half life of isotope, less stable will be the isotope.

ILLUSTRATION 6.67

Radium has atomic weight 226 and half life of 1600 years. The number of disintegrations produced per second from one gram is

- **a.** 4.8×10^{10}
- **b.** 3.7×10^{20}
- c. 9.2×10^6
- d. 3.7×10^8

Sol. b. Rate
$$\left(\frac{-\partial N}{\partial t}\right) = KN$$
 (Number of atoms of element undergoing decay)

$$\therefore \frac{-\partial N}{\partial t} = \frac{0.693}{t_{1/2}} \times \frac{\text{Mass}}{\text{Atomic mass}} \times \text{Avogadro's number}$$
$$= \frac{0.693}{1600} \times \frac{1}{226} \times 6.023 \times 10^{23}$$

$$\therefore \frac{-\partial N}{\partial t} = 3.7 \times 10^{20}$$

ILLUSTRATION 6.68

A sample of radioactive isotope with a half life of 20 days weighs 1 g. After 40 days the weight of the remaining element is

- a. 0.5 g
- **b.** 0.0 g
- c. 0.25 g
- d. 1/6 g

Sol. c.
$$t_{1/2} = 20$$
 days

$$T = 40 \text{ days}$$

$$\therefore \text{ Number of half life} = \frac{T}{t_{1/2}} = \frac{40}{20} = 2$$

$$N = \left(\frac{1}{2}\right)^n N_0 = \left(\frac{1}{2}\right)^2 \times 1 = \frac{1}{4} = 0.25 \text{ g}$$

LUSTRATION 6.69

one gram of Ra²²⁶ has an activity of nearly 1 Ci. the half life

- a. 1500 year
- b. 300 year
- c. 1582 year
- d. 200 year

c. We know

Activity =
$$\frac{0.693}{t_{1/2}} \times \frac{W}{\text{Atomic weight}} \times 6.023 \times 10^{23}$$

$$3.7 \times 10^{10} = \frac{0.693}{t_{1/2}} \times \frac{1}{226} \times 6.023 \times 10^{23}$$

$$t_{1/2} = 1582 \text{ year}$$

ILLUSTRATION 6.70

Achemist prepares 1.00 g of pure 6C11. This isotopes has half life of 21 min, decaying by the equation:

$$_{5}C^{11} \longrightarrow {}_{5}B^{11} + {}_{1}e^{0}$$

- a. What is the rate of disintegration per second (dps) at start?
- b. What is the activity and specific activity of 6C11 at start?
- c. How much of this isotope (6C11) is left after 24 hr of its preparation?

a. Applying
$$-\frac{dN}{dt} = \lambda N_0$$

= $\frac{0.693}{21 \times 60} \times \frac{1 \times 6.02 \times 10^{23}}{11}$
= 3×10^{19} dps

b. Activity =
$$\frac{3 \times 10^{19}}{3.7 \times 10^{10}}$$
 (1 curie = 3.7 × 10¹⁰ dps)

=
$$8.108 \times 10^8$$
 curie
 Specific activity = $3 \times 10^{19} \times 10^3 = 3 \times 10^{22}$ dis (kg s)⁻¹

$$= 8.108 \times 10^{11} \text{ curie}$$

$$t \quad 24 \times 60 = 68.57$$

c. Applying
$$N = N_0 \left(\frac{1}{2}\right)^n$$
 $\left[n = \frac{t}{t_{1/2}} = \frac{24 \times 60}{21} = 68.57\right]$

$$N = 1 \times \left(\frac{1}{2}\right)^{68.57} = 2.29 \times 10^{-21} \text{ g}$$

ILLUSTRATION 6.71

A radioactive isotope Cs¹³⁷ has a half life period of 30 years. Starting with 1 mg of Cs¹³⁷ how much would remain after

Total time = 120 year

We know
$$T = n \times t_{1/2}$$

or
$$120 = n \times 30$$

$$T = \text{Total time}$$

$$n = \text{Number of half lives}$$

$$n = 4$$

 \therefore Amount left after *n* half-life period $(N) = \left(\frac{1}{2}\right)^n N_0$

 $[N_0 = initial amount of radioactive element]$

$$\therefore N = \left(\frac{1}{2}\right)^4 N_0 = \left(\frac{1}{2}\right)^4 \times 1 \qquad [N_0 = 1 \text{ mg given}]$$

$$[N_0 = 1 \text{ mg given}]$$

$$N = \frac{1}{16} = 0.0625 \text{ mg}$$

ILLUSTRATION 6.72

If in 3160 years, a radioactive substance becomes one-fourth of the original amount, find its half-life period.

Sol. Given that
$$\frac{N}{N_0} = \frac{1}{4}$$
 ...(i)

We know that
$$N = \left(\frac{1}{2}\right)^n N_0$$

or
$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$
 ...(ii)

Equating Eqs. (i) and (ii), we get

$$\frac{1}{4} = \left(\frac{1}{2}\right)^n$$

$$\Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n$$

$$\therefore n=2$$

Total time $(T) = n \times t_{1/2}$

$$3160 = 2 \times t_{1/2}$$

or
$$t_{1/2} = \frac{3160}{2} = 1580$$
 year

ILLUSTRATION 6.73

A radioisotope has $t_{1/2} = 3$ years. After a given amount decays for 12 years, what fraction of the original isotope remains?

Sol. Given half life $(t_{1/2}) = 3$ year

Time for decay (T) = 12 years

We know that $T = n \times t_{1/2}$

$$12 = n \times 3$$

$$\therefore n = \frac{12}{2} = 4$$

Let the original amount N_0 .

Let the amount left after three half-life periods be N.

We know that
$$N = \left(\frac{1}{2}\right)^n N_0$$

or
$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

ILLUSTRATION 6.74

A radioactive element has half-life period of 30 days. How much of it will be left after 90 days?

Half life $(t_{1/2}) = 30$ days

We know that

Total time = $n \times t_{1/2}$

So,
$$90 = n \times 30$$

$$n = 3$$

Thus, quantity left after three half-life periods

$$= \left(\frac{1}{2}\right)^3 N_0 \qquad [N_0 = \text{original amount}]$$
$$= \frac{1}{8} \times N_0 = \frac{1}{8} N_0$$

ILLUSTRATION 6.75

The half-life period of ₈₄Po²¹⁰ is 140 days. In how many days 1 g of this isotope is reduced to 0.25 g?

Sol. Original quantity of the isotope $(N_0) = 1$ g Final quantity of the isotope N = 0.25 g

We know that,
$$N = \left(\frac{1}{2}\right)^n N_0$$

So,
$$\frac{1}{4} = \left(\frac{1}{2}\right)^n \times 1$$

or
$$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n$$

or
$$n=2$$

Time taken $T = n \times t_{1/2} = 2 \times 140 = 280 \text{ days}$

ILLUSTRATION 6.76

Calculate the average life of a radioactive substance whose half-life period is 100 years.

Sol. Given
$$t_{1/2} = 100$$
 years

We know that average life =
$$1.44 \times t_{1/2}$$

= 1.44×100
= 144 years

ILLUSTRATION 6.77

The activity of a sample of radioactive element X^{100} is 6.02 curie. Its decay constant is 3.7×10^4 s⁻¹. The initial mass of the sample will be

c.
$$10^{-20}$$
 g

b.
$$10^{-8}$$
 g **c.** 10^{-20} g **d.** 10^{-15} g

Sol. d. We know that

Activity =
$$K \times \frac{W}{\text{Atomic weight}} \times 6.023 \times 10^{23}$$

Given activity = 6.02 curie or
$$6.02 \times 3.7 \times 10^{10}$$
 s⁻¹

$$\therefore 6.02 \times 3.7 \times 10^{10} = 3.7 \times 10^4 \times \frac{W}{100} \times 6.023 \times 10^{23}$$
 or $W = 10^{-15}$ g

ILLUSTRATION 6.78

The time of decay for the nuclear reaction is given by $t = 5t_{1/2}$. The relation between average life λ and time of decay (t) is

$$\mathbf{a}$$
. $3\lambda \ln 2$

b.
$$4\lambda \ln 2$$

d.
$$6\lambda \ln 2$$

Sol. c. Given
$$t = 5t_{1/2} = 5 \times \frac{\ln 2}{K}$$

$$\left[t_{1/2} = \frac{0.693}{K} = \frac{\ln 2}{K} \right]$$

$$\therefore t = 5\lambda \ln 2$$

$$\left[\lambda = \frac{1}{K}\right]$$

ILLUSTRATION 6.79

A certain radioisotope $_{\mathbf{Z}}X^{\mathbf{A}}$ (half-life = 10 days) decays to give $_{Z-2}$ Y^{A-4}. If 1.0 g atom of $_{Z}$ X^A is kept in a sealed vessel, how much helium will accumulate in 20 days?

Sol. Decay of one atom of $_{Z}X^{A}$ to $_{Z-2}Y^{A-4}$ produces one helium atom. Hence, decay of 1 g atom of XA will produce 1 g atom of helium gas. As the half life of X is 10 days, therefore amount decayed in 20 days = $\frac{1}{2} + \frac{1}{4} = \frac{3}{4}$ g atom 1 g atom of He = 22400 cm^3 at STP

$$\therefore \frac{3}{4}$$
 g atom of He = 22400 × $\frac{3}{4}$ = 16800 cm³

ILLUSTRATION 6.80

One mole of A present in a closed vessel undergoes decay as:

$$_ZA^m \longrightarrow _{Z\rightarrow 4}B^{m-8} + 2(_2He^4)$$

What will be the volume of helium gas collected at STP after 20 days $(t_{1/2} \text{ of A} = 10 \text{ days})$?

Sol. We know that

$$N = N_0 \left(\frac{1}{2}\right)^n$$

where N = remaining mole of A; n = number of half

$$N = 1\left(\frac{1}{2}\right)^2 = \frac{1}{4}$$

$$N = 1\left(\frac{1}{2}\right)^2 = \frac{1}{4} \qquad \qquad \left[T = nt_{1/2} \implies n = \frac{T}{t_{1/2}} = \frac{20}{10}\right]$$

Number of decayed moles = $1 - \frac{1}{4} = \frac{3}{4}$

Number of moles of helium formed

 $= 2 \times \text{Number of decayed moles of A}$

$$=2\times\frac{3}{4}=\frac{3}{2}$$

Volume of helium at STP =
$$\frac{3}{2} \times 22.4 = 33.6 \text{ L}$$

One mole of X present in a closed vessel undergoes decay as:

$$_{Z}X^{A} \longrightarrow _{Z-2}Y^{A-4} + (_{2}He^{4})$$

What will be the volume of helium gas collected at SATP and What while STP (1 bar pressure, 273 K temperature) after 20 days ($t_{1/2}$ of A = 10 days?



$$N = N_0 \left(\frac{1}{2}\right)^n$$

$$\therefore N = 1 \left(\frac{1}{2}\right)^2 = \frac{1}{4}$$

$$n = \frac{T}{t_{1/2}} = \frac{20}{10} = 2$$

Number of decayed moles = $1 - \frac{1}{4} = \frac{3}{4}$

Number of moles of helium formed

= Number of decayed moles of A

$$=\frac{3}{4}$$

Volume of helium at SATP (1 atm, 298 K)

$$=\frac{3}{4}\times24.4=18.3$$
 L

Volume of helium at STP (1 bar, 273 K)

$$= \frac{3}{4} \times 22.7 = 16.8 \,\mathrm{L}$$

ILLUSTRATION 6.82

What mass of Ra²²⁶ whose $t_{1/2} = 1620$ years will give the activity of 1 millicurie?

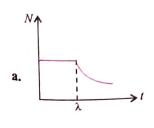
Sol. Activity =
$$\frac{0.693}{t_{1/2}} \times \frac{W}{\text{Atomic weight}} \times 6.023 \times 10^{23}$$

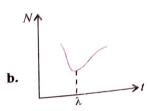
 $3.7 \times 10^7 = \frac{0.693}{1620 \times 365 \times 24 \times 3600} \times \frac{W}{226} \times 6.023 \times 10^{23}$

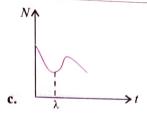
or
$$W = 10^{-3} \text{ g}$$

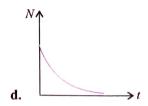
LLUSTRATION 6.83

A radioactive substance consists of two distinct species having equal number of atoms initially. The mean life of one species is λ and that of the other is 5λ . The decay products in both cases are Stable. A plot is made of total number of radioactive nuclei as a function of time. Which of the following figures best represents the form of this plot?









Sol.

d. The decrease of radioactive element (parent element) follows the exponential functions.

ILLUSTRATION 6.84

In a sample of radioactive material, what fraction of the initial number of active nuclei will remain undisintegrated after half of a half-life of the sample?

a.
$$\frac{1}{4}$$

a.
$$\frac{1}{4}$$
 b. $\frac{1}{2\sqrt{2}}$ **c.** $\frac{1}{\sqrt{2}}$ **d.** $\sqrt{2}-1$

c.
$$\frac{1}{\sqrt{2}}$$

d.
$$\sqrt{2} - 1$$

Sol. c.
$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \left(\frac{N_0}{N} \right)$$
$$\frac{2.303 \times \log 2}{t_{1/2}} = \frac{2.303}{(t_{1/2}/2)} \log_{10} \left(\frac{N_0}{N} \right)$$
$$\log_{10}(2^{1/2}) = \log_{10} \left(\frac{N_0}{N} \right)$$
$$\left(\frac{N}{N_0} \right) = \frac{1}{\sqrt{2}}$$

ILLUSTRATION 6.85

If 75% of a first-order reaction is completed in 32 min, than 50% of the reaction would complete in?

- a. 24 min
- b. 16 min

c. 8 min

d. 4 min

Sol. b. Use direct formula
$$\frac{t_{x\%}}{t_{y\%}} = \frac{\log \frac{a}{a-x}}{\log \frac{a}{a-y}}$$

$$\therefore \frac{t_{50\%}}{t_{75\%}} = \frac{\log \frac{100}{100 - 50}}{\log \frac{100}{100 - 75}} \implies t_{50\%} = \frac{t_{75\%}}{2}$$

$$t_{50\%} = \frac{32}{2} = 16 \text{ min}$$

ILLUSTRATION 6.86

1.0 g of a radioactive isotope left 125 mg after 24 hr. The halflife period of the isotope is

- a. 8 hr
- **b.** 24 hr
- c. 6 hr
- d. 4 hr

Sol. a.
$$N = \left(\frac{1}{2}\right)^n N_0 \Rightarrow 125 \text{ mg} = \left(\frac{1}{2}\right)^n 1000$$

$$\therefore \frac{125}{1000} = \left(\frac{1}{2}\right)^n \Rightarrow \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n \Rightarrow n = 3$$

Using
$$T = nt_{1/2}$$
; $t_{1/2} = \frac{24}{3} = 89 \text{ hr}$

ILLUSTRATION 6.87

If the amount of a radioactive substance is increased three times, the number of atoms disintegrated per unit time would

- a. Be double
- b. Be triple
- c. Remain one-third
- d. Not change
- **Sol. b.** Rate of disintegration $\propto N$

ILLUSTRATION 6.88

Three-fourth of a radioactive material decays in 2.5 days. How long will it take for 15/16th of the material to decay?

- a. 2 days
- b. 5 days
- c. 7.5 days
- **d.** 10 days

Sol. b.
$$\frac{t_{15/16}}{t_{3/4}} = \frac{\log \frac{a_0}{a_0 - x}}{\log \frac{a_0}{a_0 - x_1}} = \frac{\log \frac{a_0}{a_0/16}}{\log \frac{a_0}{a_0/14}} \Rightarrow \frac{\log 16}{\log 4} = \frac{4}{2}$$

$$\therefore t_{15/16} = t_{3/4} \times 2$$
$$= 2.5 \times 2 = 5$$

ILLUSTRATION 6.89

Which of the following radio-isotopes would you use to date an object containing each one of them if the object is expected to be about 100 years old?

a. Pb⁸⁷,
$$t_{1/2} = 5.7 \times 10^{10}$$
 year

b.
$$C^{14}$$
, $t_{1/2} = 5720$ year

c. Ni⁶³,
$$t_{1/2} = 92$$
 year

d.
$$H^3$$
, $t_{1/2} = 12.3$ year

Sol. c. Half life of isotope is best to calculate the age of object.

ILLUSTRATION 6.90

The half life of a radioactive element is 30 min. One-sixteenth of the original quantity of element will be left after

- **a.** 1 hr
- b. 16 hr
- c. 4 hr
- **d.** 2 hr

Sol. d. Given
$$t_{1/2} = 30 \text{ min or } \frac{1}{2} \text{ hr}$$

$$\frac{N}{N_0} = \frac{1}{16}$$

We have
$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n \Rightarrow \left(\frac{1}{16}\right) = \left(\frac{1}{2}\right)^n$$

$$\left(\frac{1}{2}\right)^4 = \left(\frac{1}{2}\right)^n \Rightarrow n = 4$$

$$T = n \times t_{1/2} = 4 \times \frac{1}{2} = 2 \text{ hr}$$

ILLUSTRATION 6.91

A sample of rock moon contains equal numbers of atoms of uranium and lead $t_{1/2}$ for U is 4.5×10^9 years. The age of rock would be

- **a.** 4.5×10^9 years
- **b.** 9.0×10^9 years
- **c.** 13.5×10^9 years
- **d.** 2.25×10^9 years

Sol. c.
$$t = \frac{2.303}{K} \log \left[1 + \frac{\text{Pb}^{206}}{\text{U}^{238}} \right]$$

$$\Rightarrow \frac{2.303 \times 4.5 \times 10^9}{0.693} \log \left[1 + \frac{\frac{1}{206}}{\frac{1}{238}} \right]$$

 $t = 13.5 \times 10^9 \text{ years}$

ILLUSTRATION 6.92

The half-life period of U^{234} is 2.5×10^5 year. In how much time is the quantity of the isotope reduced to 25% of the original amount?

Sol. Initial amount of this isotope $N_0 = 100$

Final amount of the isotope N = 25

We know that
$$N = \left(\frac{1}{2}\right)^n N_0$$

$$So25 = \left(\frac{1}{2}\right)^n \times 100$$

or
$$\frac{25}{100} = \left(\frac{1}{2}\right)^n$$

or
$$\frac{1}{4} = \left(\frac{1}{2}\right)^n$$

or
$$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n$$

or
$$n=2$$

Time taken =
$$T = n \times t_{1/2} = 2 \times 2.5 \times 10^5 = 5 \times 10^5$$
 year

Alternatively

We can use
$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log \frac{a}{a-x}}$$

$$\frac{t_{1/2}}{t_{25\%}} = \frac{0.3}{\log \frac{100}{25}}$$

$$\frac{2.5 \times 10^5}{t_{25\%}} = \frac{0.3}{\log 4}$$

or $t_{25\%}$ or time required to reduced amount to 25%

$$= \frac{2.5 \times 10^5}{0.3} \times \log 4$$
$$= \frac{2.5 \times 10^5}{0.3} \times 0.602$$
$$= 5.0 \times 10^5 \text{ years}$$

CONCEPT APPLICATION EXERCISE 6.3

Two radioactive nuclides P and Q have their decay constant in the ratio 3:2. One mole of each is taken separately and allowed to decay for a time interval of three times of half life of A. If 0.2 mol of P is left, what moles of Q will be

The mean lives of a radioactive substance are 1620 year and 405 year for α-emission and β-emission, respectively. Find out the time during which three-fourth of a sample will decay if it is decaying both by α-emission and β-emission simultaneously.

A sample of ¹⁴CO₂ was to be mixed with ordinary CO₂ for a biological tracer experiment. In order that 10³ cm³ of the diluted gas at NTP should have 10⁴ dis min⁻¹, how many µCi of radiocarbon-14 are needed to prepare 60 L of the diluted gas?

4. Sodium-24 (11 Na²⁴) is a radioactive isotope used to diagnose disease of the circulatory system. The path of Na-24 is traced by a Geiger counter after the patient drinks a tagged NaCl solution. The half life of Na-24 is 15 hr. If a patient drinks a solution containing 0.05 g of radioactive Na, how much Na will be active 60.0 hr later? How many hours would have passed if there is 3.30 × 10⁻³ g of Na-24 left?

5. A 1 mL sample of an aqueous solution containing 2 × 10⁶ counts per second of titanium is injected into the blood stream of an animal. After complete circulatory mixing, a 1-mL sample was drawn and is found to have an activity of 1.1 × 10⁴ counts per second. Calculate the blood volume of the animal.

ANSWERS

1. 0.09 **2.** 449.24 years

3. 27.03 μCi

4. (a) $K = 0.0462 \text{ hr}^{-1}$ (b) (a - x) = 0.00313 g

(c) t = 58.84 hr

5. $V = 181.8 \text{ cm}^3$

6.12 ARTIFICIAL TRANSMUTATION

Å radioactive element decays to new element with the emission of α - or β -particle. The process is spontaneous and cannot be controlled by any known method. Thus, it is possible to convert one element into another by artificial means, i.e., by the bombardment of the nuclei of the atoms with high-speed sub-atomic particles such as α -particles, β -particles, neutrons, protons, deutrons, etc.

The process of conversion of one element into another by artificial means is termed as artificial transmutation.

The first artificial transmutation was carried out by Rutherford in 1919 who bombarded nitrogen gas with alpha Particles and obtained hydrogen and oxygen.

Fig. 6.6 Artificial transmutation

The isotopes ${}_{8}O^{17}$ and ${}_{1}H^{1}$ are stable and no further disintegration takes place. The subatomic particles used for bombarding the nuclei are called bombarding particles or projectiles.

The positively charged particles such as α -particles, protons, etc., had the limitation that they are repelled by the positively charged nuclei of the atoms being bombarded (especially with high atomic numbers). On the other hand, β -rays were also not so effective because of their small mass. These charged particles can be made more effective by accelerating to very high speeds by fluctuating electric and magnetic fields in machines such as cyclotron, synchrotron, etc. (Fig. 6.7). These high-speed particles are more efficient in causing nucleus to disintegrate an impact.

The discovery of neutron by Chadwick, in 1932, added another projectile for transmutation. The neutron being electrically neutral can penetrate easily into the atomic nucleus. Although neutrons are the most effective and versatile of projectiles, yet they suffer the objection that they must be produced by the transmutation at the time of use. High-speed neutrons are obtained when beryllium-9 is bombarded with α -particles,

 $_4\mathrm{Be^9} + _2\mathrm{He^4} \longrightarrow {}_6\mathrm{C^{12}} + _0n^1$ and slow neutrons are obtained by bombarding lithium-7 with protons,

$$_{3}\text{Li}^{7} + _{1}\text{H}^{1} \longrightarrow {}_{4}\text{Be}^{7} + {}_{0}n^{1}$$

In general, for the transmutation of lighter elements, charged particles such as alpha particles, protons, and deuterons are used while for heavier elements, neutrons are used.

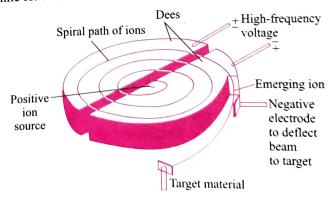


Fig. 6.7 Cyclotron

Principle of cyclotron: It consists of two hollow D-shaped plates called *dees* which are separated by a gap and work as electrodes. The dees are enclosed in an evacuated chamber which is placed between the poles of a powerful electromagnet, one above and the other below the dees. Using a high-frequency voltage

from a generator, the dees are kept oppositely charged, alternately positive and negative. The ion source is located between the dees. Under the influence of the magnetic and electric fields, the ions move from the source and are accelerated to follow a spiral path (Each time the ions reach the gap between the dees, the polarity of the dees is reversed. Thus, positively charged particles are pushed out of the positive dee and attracted into the negative dees.). At the end of their path, the ions encounter a negative electrode that deflect them to a target material.

Some typical transmutations revolving various particles are summarized below:

a. Alpha-particle-induced reactions:

$$_{4}\text{Be}^{9} + _{2}\text{He}^{4} \longrightarrow {}_{6}\text{C}^{12} + {}_{0}n^{1}$$

Since α -particle is used and a neutron is produced, the reaction may be termed as (α, n) reaction. In another α -bombardment nuclear reaction, the isotope produced is itself radioactive. Thus,

$$_{13}Al^{27} + _{2}He^{4} \longrightarrow _{15}P^{30} + _{0}n^{1}$$

The isotope $_{15}P^{30}$ undergoes decay by positron (β^{\oplus}) emission:

$$_{15}P^{30} \longrightarrow {}_{14}Si^{31} + \beta^{\oplus}$$

This was the first example of radioactivity produced by artificial means.

b. Deuteron-induced reactions:

i.
$${}_{6}C^{12} + {}_{1}H^{2} \longrightarrow {}_{7}N^{13} + {}_{0}n^{1}$$

$$(D, n)$$
 reaction

ii.
$$_{8}O^{16} + _{1}H^{2} \longrightarrow _{7}N^{14} + _{2}He^{4}$$

$$(D, \alpha)$$
 reaction

c. Proton-induced reactions:

i.
$$_{7}N^{14} + _{1}H^{1} \longrightarrow {_{8}O^{15}} + \gamma$$

$$(p, \gamma)$$
 reaction

ii.
$$_3\text{Li}^7 + _1\text{H}^1 \longrightarrow _2\text{He}^4 + _2\text{He}^4$$

$$(p, \alpha)$$
 reaction

d. Neutron-induced reactions:

i.
$$_{11}Na^{23} + _{0}n^{1} \longrightarrow _{11}Na^{24} + \gamma$$

$$(n, \gamma)$$
 reaction

ii.
$$_{52}\text{Te}^{131} + _{0}n^{1} \longrightarrow _{53}\text{P}^{132} + _{-1}e^{0}$$

$$(n, \beta^{\odot})$$
 reaction

iii.
$$_{7}N^{14} + _{0}n^{1} \longrightarrow {}_{6}C^{14} + _{1}H^{1}$$

$$(n, p)$$
 reaction

Some of the isotopes produced as a result of neutron bombardment find applications in different areas of radioactivity. The preparation of isotopes of elements beyond uranium involves many neutron-induced reactions.

6.13 NUCLEAR REACTION

A nuclear reaction represents the transformation of one stable nucleus into another nucleus by bombarding the former with suitable high-energy particles.

Nuclear reactions are expressed in the same fashion as chemical reaction, i.e., reactant on left hand side and product on the right hand side of the sign of (=) or (\rightarrow) .

For example, a nuclear reaction

$$_{2}H^{4} + _{7}N^{14} \longrightarrow {_{8}O^{17}} + _{1}H^{1}$$

· is represented as $_7N^{14}$ (α , p) $_8O^{17}$, where $_7N^{14}$ denotes that it is a target, α -practicle is a projectile, proton (p) is the particle emitted and $_8O^{17}$ is the product. In nuclear reaction, Q is the total energy change in the reaction. It is called *nuclear energy* or Q value of the reaction.

Difference between a chemical reaction and a nuclear reaction. Some important points in which nuclear reactions differ from chemical reactions are given in Table 6.4.

Table 6.4 Difference between a chemical reaction and a nuclear reaction

Chemical reaction	Nuclear reaction
a. In these reactions, only the electrons of the outermost shells of the atoms are involved.	a. In these reactions, the nucle of the atoms are involved.
b. Here some bonds are broken and some new bonds are formed.	b. Nuclear reactions do not involve any breaking or making of bonds.
c. In such reactions, the energy may be evolved or absorbed.	c. In such reactions, energy is always evolved.
d. The energy evolved or absorbed is not very high.	d. In some nuclear reactions, the energy evolved is very high (may be million times greater than those in ordinary chemical reactions).
e. The rate of these reactions are affected by temperature, pressure, etc.	e. The rate of these reactions are not affected by temperature, pressure, etc.
f. These reactions may be reversible in some cases.g. No new element can be produced.	f. These reactions are irreversible.g. Element may be converted from one to another.

6.13.1 Types of Nuclear Reactions

a. Projectile capture reactions: The bombarding particle is absorbed with or without the emission of γ -radiations.

$${}_{92}{\rm U}^{238} + {}_{0}n^{1} \longrightarrow {}_{92}{\rm U}^{239} + \gamma$$

$${}_{13}{\rm Al}^{27} + {}_{0}n^{1} \longrightarrow {}_{13}{\rm Al}^{28} + \gamma$$

b. Particle-particle reactions: Majority of nuclear reactions come under this category. In addition to the product nucleus, an elementary particle is also emitted.

$${}_{11}Na^{23} + {}_{1}H^{1} \longrightarrow {}_{12}Mg^{23} + {}_{0}n^{1}$$

$${}_{11}Na^{23} + {}_{2}He^{4} \longrightarrow {}_{12}Mg^{26} + {}_{1}H^{1}$$

$${}_{7}N^{14} + {}_{0}n^{1} \longrightarrow {}_{6}C^{14} + {}_{1}H^{1}$$

c. Spallation reactions: High-speed projectiles with energies approximately 40 MeV may chip fragments from a heavy nucleus, leaving a smaller nucleus.

$${}_{29}\text{Cu}^{63} + {}_{2}\text{He}^4 + 400 \text{ MeV} \longrightarrow {}_{17}\text{Cl}^{37} + 14 {}_{1}\text{H}^1 + 16 {}_{0}^{n^1}$$
 ${}_{92}\text{U}^{238} + {}_{2}\text{He}^4 \longrightarrow {}_{74}\text{W}^{187} + 20 {}_{1}\text{H}^1 + 35 {}_{0}^{n^1}$

d. Fission reactions: A reaction in which a heavy nucleus is broken down into two or more medium heavy fragments. The process is usually accompanied with the emission of neutrons and large amount of energy.

$$_{92}U^{235} + _{0}n^{1} \longrightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 3{}_{0}n^{1} + 200 \text{ MeV}$$

Fusion reactions: Light nuclei fuse together to reproduce comparatively heavier nuclei.

comparation
$$_{2}^{\text{comparation}}$$

 $_{1}^{\text{H}^{2}}+_{1}^{\text{H}^{3}}\longrightarrow _{2}^{\text{He}^{4}}+_{0}^{n^{1}}+17.6 \text{ MeV}$

A fusion reaction is the source of tremendous amount of

Artificial or Induced Radioactivity

ion.

 v_{0}

Curie (daughter of Marie Curie) and her husband F. Joliot 1934 found that when aluminium, boron, and magnesium were mbarded with α-particles, the products formed were radioactive which disintegrated spontaneously with the emission of positrons which are positively charged electrons, $+1e^0$). For example, for the reaction may be represented as

He⁴ +
$$_{13}$$
Al²⁷ \longrightarrow $_{15}$ P³⁰ + $_{0}$ n¹

Radioactive isotope
$$\downarrow t_{1/2} = 2.55 \text{ min}$$

$$_{14}$$
Si³⁰ + $_{14}$ e⁰ (positron)

The phenomenon in which the artificial disintegration of a stable nucleus leads to the formation of a radioactive isotope is called artificial radioactivity or induced radioactivity.

The radioactive isotopes formed by the artificial transmutation have usually very short half-life periods; they are rarely found in nature. This is because as soon as they are formed, they decay off.

In some cases, instead of positrons, electrons (β-particles) are emitted by the artificial radioactive isotopes produced.

A few examples of the bombardment reactions leading to the formation of radioactive isotope are given below:

a. Those involving bombardment with α -particles, e.g.,

$$_{2}\text{He}^{4} + _{12}\text{Mg}^{24} \longrightarrow {}_{14}\text{Si}^{27} + {}_{0}n^{1}$$

$$_{14}\text{Si}^{27} \longrightarrow {}_{13}\text{Al}^{27} + {}_{+1}e^0$$

Stable Positron

$$_{2}\text{He}^{4} + _{5}\text{B}^{10} \longrightarrow {}_{7}\text{N}^{13} + {}_{0}n^{1}$$

$$_{7}N^{13} \longrightarrow {}_{6}C^{13} + {}_{+1}e^{0}$$

Stable Positron

b. Those involving bombardment with protons, e.g.,

$$_{1}^{H^{1}} + _{6}^{C^{12}} \longrightarrow _{7}^{N^{13}}$$

$$7^{N^{13}} \longrightarrow {}_{6}C^{13} + {}_{+1}e^{0}$$

Stable Positron

c. Those involving bombardment with deuterons, e.g.,

$$_{1}^{D^{2}}+_{11}^{}Na^{23}\longrightarrow {}_{11}^{}Na^{24}+_{1}^{}H^{1}$$

$$^{11}\text{Na}^{24} \longrightarrow {}_{12}\text{Mg}^{24} + {}_{-1}e^0$$

Stable Electron

d. Those involving bombardment with neutrons, e.g.,

$$_{11}$$
Na²⁴ \longrightarrow $_{12}$ Mg²⁴ + $_{-1}$ e⁰

Stable Electron

$$_{13}\text{Al}^{27} + _0 n^1 \longrightarrow _{11} \text{Na}^{24} + _2 \text{He}^4$$
Radioactive

It may be pointed out here that the artificially produced radioactive elements behave exactly in the same way as the natural radioactive elements, i.e., they follow the same disintegration rate equation and have constant half-life periods. However, they differ only in the fact that whereas natural radioactivity is exhibited only by elements with high atomic numbers (>83), the artificial radioactivity can be induced even in elements with low atomic numbers.

6.14 SYNTHETIC ELEMENTS INCLUDING TRANSURANICS

Elements with atomic number (Z) greater than 92, i.e., Z >92 do not exist naturally on the earth because no isotope of these elements is stable. The elements coming after uranium (Z = 92) are called transuranium or transuranic elements. As nuclear stability decreases with increase in atomic number, hence it was thought that it would not be possible to study element with Z > 100, as their half life will be too small. However, after the discovery of nuclear reaction most of the elements with atomic number (Z) > 92 have been synthesized by artificial transmutation, hence they are called synthetic elements. For example, elements with atomic number (Z) ranges between 104 and 109 have been reported recently and are d-block elements. These are called transactinides or superheavy elements, as the actinide series is complete at element with Z = 103 (lawrencium).

The nuclear reactions which are employed to synthesize some of these elements are given below:

a. Technetium:

$$_{42}\text{Mo}^{96} + _{1}\text{H}^{2} \longrightarrow _{43}\text{Tc}^{97} + _{0}n^{1}$$

b. Neptunium and plutonium:

$${}_{92}U^{238} + {}_{0}n^{1} \longrightarrow {}_{92}U^{239} + \gamma$$

$${}_{92}U^{239} \xrightarrow{-\beta^{\odot}} {}_{93}Np^{239} \xrightarrow{-\beta^{\odot}} {}_{94}Pu^{239}$$

 $_{0.4}$ Pu²³⁹ is an α -emitter with half life of 2.4 × 10⁴ years.

c. Americium and curium

$$\begin{array}{l} {}_{94}\mathrm{Pu^{239}} + {}_{0}n^{1} \longrightarrow {}_{94}\mathrm{Pu^{240}} + \gamma \\ {}_{94}\mathrm{Pu^{240}} + {}_{0}n^{1} \longrightarrow {}_{94}\mathrm{Pu^{241}} + \gamma \\ {}_{94}\mathrm{Pu^{241}} \longrightarrow {}_{95}\mathrm{Am^{241}} + \beta ^{\odot} \end{array}$$

$$_{94}\text{Pu}^{239} + _{2}\text{He}^{4} \longrightarrow _{96}\text{Cm}^{242} + _{0}n^{1}$$

d. Berkelium and californium:

$$_{95}\text{Am}^{241} + _{2}\text{He}^{4} \longrightarrow _{97}\text{Bk}^{243} + 2_{0}n^{1}$$

 $_{96}\text{Cm}^{242} + _{2}\text{He}^{4} \longrightarrow _{98}\text{Cf}^{245} + _{0}n^{1}$

e. Later elements:

Bombardment with heavier nuclides produces later elements. For example:

$$_{96}\text{Cm}^{246} + {}_{6}\text{C}^{12} \longrightarrow {}_{102}\text{No}^{254} + 4 {}_{0}n^{1}$$
Nobelium

$$_{98}\text{Cf}^{250} + _{5}\text{B}^{11} \longrightarrow _{103}\text{Lr}^{257} + 4_{0}n^{1}$$
Lawrencium

Many of the heavier isotopes are short lived. The longest lived isotope of fermium, for example, is 100 Fm²⁵⁴ with half-life of 3.3 hr. Thus (to mention the most stable isotopes), 95 Am²⁴¹ and 60 Cm²⁴⁴ are available in grams, 97 Bk²⁴⁹, 98 Cf²⁴⁹, and 98 Cf²⁵¹ in milligrams, 99 Es²⁵³ (einsteinium) in micrograms and the elements beyond einsteinium only in few atoms. It may be pointed out that so far, elements upto atomic numbers 109 have been identified.

Theoretical calculations on the stability of the nuclei predict that elements with an even number of protons in the nucleus are usually more stable than their neighbours with odd atomic numbers, i.e., they are less likely to decay. Also nuclei with both an even number of protons and even number of neutrons are more likely to be stable. A nucleus is more stable if number of neutrons or protons is 2, 8, 20, 28, 50, 82, 114, 126, 164, and 184. These are called *magic numbers*. The stability is particularly high if both the number of protons and neutrons are magic numbers. For example, 82 Pb²⁰⁸ is very stable with protons 82 and neutrons 126 (208 – 82). Thus, on this basis, we accept 114 Uuq²⁷⁸, 114 Uuq²⁹⁸, and 126 Ubh³¹⁰ to be stable enough to exist.

6.15 NUCLEAR FISSION

Nuclear fission is the phenomenon of splitting of a heavy nucleus into two lighter nuclei of nearly comparable masses with release of a large amount of energy. In 1939, Hahn and Strassmann observed that out of the three natural isotopes of uranium, $_{92}\mathrm{U}^{238},\,_{92}\mathrm{U}^{235},\,$ and $_{92}\mathrm{U}^{234},\,$ the $_{92}\mathrm{U}^{235}$ nucleus undergoes nuclear fission when bombarded with slow neutrons. The $_{92}\mathrm{U}^{236}$ isotope formed breaks up in several different ways, for example,

$${}_{56}Ba^{140} + {}_{36}Kr^{93} + 3{}_{0}n^{1}$$

$${}_{54}Xe^{144} + {}_{38}Sr^{90} + 2{}_{0}n^{1}$$

$${}_{55}Co^{144} + {}_{37}Rb^{90} + 2{}_{0}n^{1}$$

During fission, there is always a loss of mass which is converted into energy according to Einstein equation $E = mc^2$. There is a loss of about 0.223 amu mass during one fission. Thus, energy released in one fission is equal to 0.223 \times 931, i.e., 208 MeV.

Calculation of the energy released

In fission reaction, the sum of masses of the fragments and the neutrons released is less than the sum of one uranium atom and one neutron. The mass thus lost is converted into energy according to the Einstein equation

where m is the mass lost and c is the velocity of light.

Mass of 1 amu =
$$\frac{1}{12}$$
 th of the mass of an atom of carbon
= $\frac{1}{12} \times \frac{12}{6.023 \times 10^{23}}$
= 1.6606×10^{-27} kg
Velocity of light (c) = 2.9979×10^8 m s⁻¹

Therefore, substituting values in Eq. (i), $E = (1.6606 \times 10^{-27}) \times (2.9979 \times 10^{8})^{2} \text{ J}$ $= 1.4924 \times 10^{-10} \text{ J}$ Energy in eV = $\frac{1.4929 \times 10^{-10}}{1.6022 \times 10^{-19}} \text{ eV}$ $[\because 1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J}]$ $= 931.48 \times 10^{6} \text{ eV}$ = 931.48 MeV $[1 \text{ MeV} = 10^{6} \text{ eV}]$

Now the energy released when one atom of uranium undergoes nuclear fission according to the following reaction can be calculated as under:

Actual isotopic masses
$$\frac{{}_{92}U^{235} + {}_{0}n^{1}}{Total = 236.069 u}$$

$$\longrightarrow {}_{56}Ba^{144} + {}_{36}Kr^{90} + 2 {}_{0}n^{1}$$
Actual isotopic masses
$$\frac{143.881 \quad 89.947 \quad 2 \times 1.009}{Total = 235.846 \text{ amu}}$$

Loss of mass (m) = 236.069 - 235.846 = 0.223 amu

: Energy released during fission of one U-atom

$$= 0.223 \times 931.5 \text{ MeV} = 208 \text{ MeV}$$

As 1 g of U-235 = $(6.022 \times 10^{23})/235$ atoms, therefore energy released when 1 g of U-235 undergoes fission

$$= 208 \times \frac{6.022 \times 10^{23}}{235} \text{ MeV}$$
$$= 5.33 \times 10^{23} \text{ MeV}$$

Thus, a tremendous amount of energy is released.

6.15.1 CHAIN REACTION

The fission of $_{92}U^{235}$ by thermal or slow moving neutron is represented as

$$_{92}U^{235} + _{0}n^{1} \longrightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 3 {}_{0}n^{1} + Q$$

Now, the three secondary neutrons produced in the reaction may bring about the fission of three more $_{92}\mathrm{U}^{235}$ nuclei and produce nine neutrons which in turn can bring about the fission of nine $_{92}\mathrm{U}^{235}$ nuclei and so on. Thus, a continuous reaction called nuclear chain reaction would start and a huge amount of energy will be released in a short time. The chain reaction is shown in Fig. 6.8.

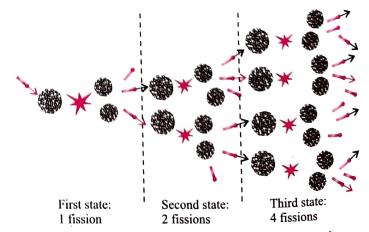


Fig. 6.8 Schematic view of the start of a fission chain reaction

Following factors should be considered for a self- propagating agetion:

Critical size: For a chain reaction to continue, the fissionable material (uranium-235) must have a minimum size. If the size is smaller than this minimum size, the neutrons escape from the sample without hitting the nucleus and thus the chain reaction stops.

The minimum mass which the fissionable material must have so that one of the neutrons released in every fission hits another nucleus and causes fission so that the chain reaction continues at a constant rate is called *critical mass*. If the mass is less than the critical mass, it is called *sub-critical*. If the mass is more than the critical mass, it is called *super-critical*. In this case, many of the neutrons released in every fission are able to hit the other nuclei and thus the number of fissions multiply in the chain reaction. The shape and the density of packing of the material are also significant for the nuclear fission. The critical mass of U-235 is between 1 and 100 kg.

- b. Leakage of neutron from the system: Some of the secondary neutrons produced may escape out of the system and do not take part in further fission. Leakage can be reduced by proper designing of system.
- c. Absorption of neutron by impurities: The secondary neutrons may be absorbed by impurities which are not fissionable. This loss may be reduced by having a fissionable material free from impurities.

6.15.2 APPLICATION OF NUCLEAR FISSION

In nuclear fission reaction, a tremendous amount of energy is released. If it is uncontrolled, it can be used for destructive purpose, e.g., in the formation of atom bomb. If the chain reaction is controlled, the energy released can be used for constructive purpose, e.g., in the nuclear reactor.

Atomic Bomb

Pounds of fissionable material (U²³⁵ or Pu²³⁹) is taken in the form of two separate pieces; each piece is in sub-critical stage (surface area is very large, i.e., loss of neutrons is high). One piece is called wedge and the other target. At the time of explosion, these pieces are driven together rapidly by using explosives such as TNT (trinitro toluene) lying behind each of U²³⁵ pieces as to make one large piece of fissionable material. At this instant, the over-critical stage is achieved and a fast chain reaction is set up. This results in a violent explosion with the release of tremendous amount of thergy. Figure 6.9 shows one of the designs of atomic bomb.

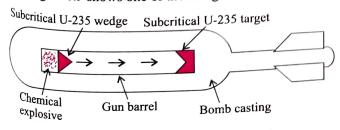


Fig. 6.9 A simple design of an atomic bomb

Nuclear Reactor

A nuclear reactor is an arrangement in which the energy produced (in the form of heat) in a nuclear fission can be used in a controlled manner to produce steam which can run a turbine and produce electricity.

A nuclear reactor has five main components (a) fuel, (b) moderator, (c) control rods, (d) coolant, and (e) shield.

The main part of the nuclear reactor called the nuclear core is shown in Fig. 6.10.

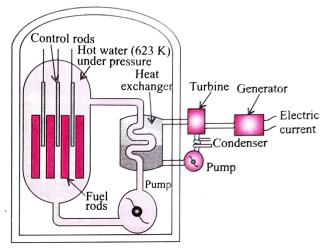


Fig. 6.10 Schematic diagram of a nuclear reactor. This one is pressurized water reactor, in which the coolant is water under pressure

- a. Nuclear fuels: Nuclear fuels are of two types:
 - i. Fissile materials: These on bombardment with slow neutrons directly produce a chain reaction leading to release of energy. These fissile materials are in use at present. These are U²³⁵, Pu²³⁹ and U²³⁹. U²³⁵ is obtained from natural sources while Pu²³⁹ and U²³³ are obtained by artificial transmutation.
 - ii. Fertile materials: A fertile material is one which by itself is non-fissile in nature, can be converted into a fissile material by reaction with neutrons. U²³⁸ and Th²³² are fertile materials. U²³⁸ is converted into Pu²³⁹ by the following nuclear reaction:

$$_{92}U^{238} + _{0}n^{1} \longrightarrow {}_{92}U^{239}* \xrightarrow{-\beta} {}_{93}Np^{239}* \xrightarrow{-\beta^{2}} {}_{91}Pu^{239}$$

Generally, enriched $_{92}U^{235}$ say 2–3% is used as nuclear fuel.

- **b. Moderator:** The moderator is used to slow down the neutrons so that they are captured and become effective to bring about fission reaction. The most commonly used moderators are graphite and heavy water (D_2O) .
- c. Control rod: Boron or cadmium steel rods are used as control rods. These rods absorb neutrons and thereby control the rate of fission, e.g.,

$$_{5}B^{10} + _{0}n^{1} \longrightarrow {_{3}Li^{7}} + _{2}He^{4}$$

d. Coolant: Liquid alloy of sodium and potassium is used as coolant; it takes away the heat to the exchanger. Heavy water, polyphenyls, and carbon dioxide have also been used scoolants.

e. Shield: To prevent the loss of heat and to protect the operators operating the reactor from the radiation and heat, the entire core is enclosed in a heavy steel or concrete dome, called the shield.

A large amount of energy released from fission is utilized in generating steam which runs the steam turbine, which produces electricity. The atomic reactor when used for production of electricity is termed *power plant*.

Spallation reactions: This is another category of nuclear reaction, which is similar to fission reaction.

Spallation reactions differ in the fact that they are brought about by high energy bombarding particles or photons. Due to high energy, a large number of particles are emitted from the target nucleus, and the product nucleus has mass number and atomic number much less than the target nucleus. For example, when U^{238} is bombarded with α -particles having energy equal to 400 MeV, it releases 6 protons and 13 neutrons, forming $_{88}Ra^{225}$ as the product nucleus, i.e., the reaction is

$$_{92}U^{238}(\alpha, 6p, 13n)_{88}Ra^{225}$$

Breeder reactors

Natural uranium contains very little (0.72%) of its fissionable isotope U^{235} and needs to be enriched in the latter to be useful as a fuel in nuclear reactor. A breeder reactor is one that produces more fissionable nuclei than it consumes. For example, when naturally more abundant isotope of uranium, $_{92}U^{238}$ is bombarded with fast neutrons, the following nuclear transmutation occurs:

$$_{92}U^{238} + _{0}n^{1} \longrightarrow _{92}U^{239} \xrightarrow{-\beta^{\odot}} _{93}Np^{239} \xrightarrow{-\beta^{\odot}} _{94}Pu^{239}$$

Here, the breeder reactor produces fissile $_{94}$ Pu²³⁹ from nonfissile uranium. Similarly, naturally more abundant isotope of thorium $_{90}$ Th²³² can be used to produce a fissible or fissionable isotope of uranium $_{92}$ U²³³. Thus,

$$_{90}\text{Th}^{232} + {}_{0}n^{1} \longrightarrow {}_{90}\text{Th}^{233} \stackrel{-\beta^{\odot}}{\longrightarrow} {}_{91}\text{Pa}^{233} \stackrel{-\beta^{\odot}}{\longrightarrow} {}_{92}\text{U}^{233}$$

In all reactors, heat from the core is extracted by heat exchangers and is used to convert water into steam. This is then used to drive turboalternators for producing electricity. In breeder reactors, an alloy of sodium and potassium is used as coolant. The liquid metal gives its heat to water in a heat exchanger.

6.16 NUCLEAR FUSION

Nuclear fusion is the phenomenon of fusing two or more lighter nuclei to form a single heavy nucleus. Just as the fission of heavy nuclei is accompanied by mass losses resulting into the liberation of large amounts of energy, the fusion of light nuclei is accompanied by mass losses and the evolution of large quantities of energy. For example, the formation of helium from hydrogen, deuterium ($_1H^2$), or tritium ($_1H^3$) is, in principle, also capable of generating immense amount of energy. Some such reactions and energy release in each process are shown below.

Fusion reaction	Mass loss	Energy released (kJ mol ⁻¹)
$_{1}H^{2} + _{1}H^{2} \longrightarrow _{2}He^{4}$	0.026	2.3 × 10 ⁹
$_{1}H^{2} + _{1}H^{3} \longrightarrow _{2}He^{4} + _{0}n^{1}$	0.018	1.79×10^{9}
$4_1H^1 \longrightarrow {}_2He^4 + 2\beta^{\oplus}$	0.029	2.6×10^{9}

The process of fusion has an advantage that unlike the process of fission large amount of highly radioactive nuclides are not obtained as byproduct whose safe disposal poses a great problem.

The nuclear fusion takes place under the condition of very high temperature ($>10^7$ K) and pressure. This is necessary as the nuclei have enough kinetic energy so that they can come closer to each other than the range of nuclear forces, against their mutual electrostatic repulsion. For this reason, fusion reactions are referred to as *thermonuclear reactions*.

In nature, high temperatures of the order of 10^6 K are available only in the sun (which has a temperature of about 15×10^6 K in its centre). Further, it is found (from spectroscopic studies) that sun contains about 73% hydrogen, 26% helium, and 1% of other elements. It is, therefore, believed that in the sun the following fusion processes have been suggested as the chief source of sun's energy:

The net effect is the conversion of four protons to give one ${}_{2}\mathrm{He^4}$ nucleus with the emission of γ -rays, two positrons, and two neutrinos.

$$4_1H^1 \longrightarrow {}_2He^4 + 2_{+1}e^0 + 2_0v^0$$

Calculations show that this process is accompanied by the evolution of about 26 MeV of energy (which is about 1/10th of that liberated in the fission of a U-235 nucleus). It is in fact this energy which is available to us from the sun and which keeps the sun at extremely high temperature.

On earth, till date, it has been possible to produce a fusion reaction only if a fission bomb is used to generate the high temperature. The principle of hydrogen bomb is explained as follows:

Hydrogen bomb: A hydrogen bomb has an arrangement of nuclear fission in the centre which is surrounded by a mixture of deuterium $\binom{1}{4}$ and lithium-6 isotope $\binom{3}{4}$ Li⁶).

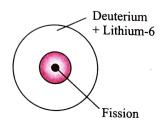


Fig. 6.11 Principle of H-bomb

The nuclear fission provides heat and neutrons. The neutrons The nuclear transmission in the neutrons of th wheat liberated is required for the fusion between 1H2 and 1H3 the fusion reactions are the accompanied by the fusion between 1H2 and 1H3 and 1H3 are the fusion reactions are the accompanied by the fusion between 1H2 and 1H3 are the fusion between 1H2 and 1H3 are the fusion reactions are the accompanied by the fusion between 1H3 and 1H3 are the fusion reactions are the accompanied by the fusion between 1H3 are the fusion between 1H3 and 1H3 are the fusion between 1 heat liberation reactions are the accompanied by the liberation amount of energy. Thus, the reactions to the liberation in a large amount of energy. Thus, the reactions taking place in a fallarge homb may be represented as follows: of a large bomb may be represented as follows:

Fission (in the centre)
$$\longrightarrow$$
 Heat + neutrons

Fission (in the centre)
$${}_{3}\text{Li}^{6} + {}_{0}n^{1} \longrightarrow {}_{1}\text{H}^{3} + {}_{2}\text{He}^{4} + 4.78 \text{ MeV}$$
Tritium

$$_{1}H^{2} + _{1}H^{3} \longrightarrow _{2}He^{4} + _{0}n^{1} + 17.6 \text{ MeV}$$

Deuterium Tritium

$${}_{1}H^{2} + {}_{1}H^{2} \longrightarrow {}_{2}He^{3} + {}_{0}n^{1} + 3.3 \text{ MeV}$$

$$_{1}^{1H^{2}+1}^{1H} \xrightarrow{}_{2}^{1H^{2}+1}^{1H} \longrightarrow _{2}^{2}^{1H}^{2} + 2_{0}^{1}^{1} + 11 \text{ MeV}$$

Tritium has to be prepared within the hydrogen bomb because it is not stable.

Though the energy liberated per fusion is smaller than the energy liberated per fission of U-235 (which is about 200 MeV), net the hydrogen bomb is much more powerful than the atom homb. The reason lies in the fact that firstly the masses per atom of deuterium and tritium are much smaller than that of uranium and secondly there are no restrictions of critical mass for fusion process to occur.

Important points of difference are given in Table 6.5.

Table 6.5 Difference between nuclear fission and nuclear fusion

Nuclear fission	Nuclear fusion
a. This process occurs in heavy nuclei	a. This process occurs in lighter nuclei.
b. The heavy nucleus splits into lighter nuclei of comparable masses	b. The lighter nuclei fuse together to form a heavy nucleus.
c. This reaction occurs at ordinary temperature.	 c. This reaction occurs at a very high temperature.
d. The energy liberated in one fission is about 200 MeV.	d. The energy liberated in one fusion is about 24 MeV.
e. This can be controlled.	e. This cannot be conrolled.
f. Products of fission are usually unstable radioactive in nature.	f. Products of fusion are usually stable and non-radioactive in nature.
g. It requires minimum size of fissionable material and if the size of material exceeds the	g. There is no limit to the size of the fuel for the reaction to start.
critical size, the	

ILLUSTRATION 6.93

reaction becomes explosive.

What do you understand by the following notations in respect of the types of artificial transmutations?

- $\mathbf{a}.(n,\beta^{\Theta})$
- **b.** (p, β^{\odot})
- $\mathbf{c.}(\alpha,n)$
- $\mathbf{d}.(D,p)$

Sol.

- **a.** The striking particle is n and the particle in the product
- **b.** The striking particle is p (proton), the particle produced
- c. The striking particle is α -particle ($_{2}$ He⁴) and one neutron is on the product side.
- d. Deuteron (1H2) is the striking particle and one proton is in the product.

ILLUSTRATION 6.94

In artificial transmutation which has stronger striking ability and why proton or neutron move with the same speed?

Sol. Neutron with its neutral character has stronger striking ability in nuclear reactions. Proton with positive charge is not so effective to attack the positively charged nucleus.

ILLUSTRATION 6.95

Complete the following nuclear equations:

a.
$$_{96}\text{Cm}^{246} + _{6}\text{C}^{12} \longrightarrow {}_{102}\text{No}^{254} +$$
b. $_{94}\text{Pu}^{239} + \longrightarrow {}_{96}\text{Cm}^{242} + {}_{0}n^{1}$

Sol

a.
$$_{96}\text{Cm}^{246} + _{6}\text{C}^{12} \longrightarrow {}_{102}\text{No}^{254} + 4 {}_{0}n^{1}$$

b. $_{94}\text{Pu}^{239} + _{2}\text{He}^{4} \longrightarrow {}_{96}\text{Cm}^{242} + {}_{0}n^{1}$

b.
$$_{94}$$
Pu²³⁹ + $_{2}$ He⁴ $\longrightarrow _{96}$ Cm²⁴² + $_{0}$ n¹

ILLUSTRATION 6.96

Calculate the energy released in the following:

$$_{1}H^{2} + _{1}H^{3} \longrightarrow _{2}He^{4} + _{0}n^{1}$$

(Given masses:
$$H^2 = 2.014$$
; $H^3 = 3.016$; $He = 4.003$; $n = 1.009 \text{ m}_{10}$)

Sol. Mass on the reactant side

$$= 2.014 + 3.016 = 5.030 \text{ m}_{\text{u}}$$

Mass on the product side

$$=4.003+1.009=5.012$$

Mass loss =
$$5.030 - 5.012 = 0.018 \text{ m}_{u}$$

Energy released per atom of helium

$$= (0.018 \times 931) \text{ MeV} = 16.76 \text{ MeV}$$

ILLUSTRATION 6.97

The beta activity of 1 g of carbon made from green wood is 15.3 counts per minute. If the activity of 1 g of carbon derived from the wood of an Egyptian mummy case is 9.4 counts per minute under the same conditions, how old is the wood of the mummy case?

$$(t_{1/2} \text{ for } C^{14} = 5770 \text{ years})$$

Sol.
$$K = 0.693/t_{1/2} = 0.693/5770$$

= $1.20 \times 10^4 \text{ year}^{-1}$

$$\log N_0/N_t = Kt/2.303$$

$$1.20 \times 10^{-4} \times t/2.303 = \log N_0/N_t$$

$$= \log 15.3/9.4$$
Hence $t = 2.303/1.20 \times 10^{-4} \log 15.3/9.4$

$$= 3920 \text{ years}$$

ILLUSTRATION 6.98

Calculate the loss in mass during the change:

$$_{3}\text{Li}^{7} + _{1}\text{H}^{1} \longrightarrow 2_{2}\text{He}^{4} + 17.25 \text{ MeV}$$

Sol. Total energy change during reaction (given) = 17.25 MeV We know that energy = mass defect
$$\times$$
 931 MeV or $E = \Delta m \times 931$

:. Mass defect
$$(\Delta m) = \frac{E}{931} = \frac{17.25}{931} = 0.0185$$
 amu

or
$$\Delta m = 0.185$$
 amu = 3.07×10^{-26} g

ILLUSTRATION 6.99

The atomic mass of Li, He, and proton are 7.01823 amu, 4.00387 amu, and 1.00715 amu, respectively. Calculate the energy evolved in the reaction.

$$_3\text{Li}^7 + _1p^1 \longrightarrow 2_2\text{He}^4 + \Delta E$$

Given 1 amu = 931 MeV.

Sol. Mass of reactant = Mass of Li + Mass of
$$p$$

= $7.01823 + 1.00715 = 8.02538$ amu

Mass of products =
$$2 \times Mass$$
 of He

$$= 2 \times 4.00387 = 8.00774$$
 amu

$$\therefore$$
 Mass loss during change = $8.02538 - 8.00774$
= 0.01764 amu

ILLUSTRATION 6.100

Calculate the energy released in joules and MeV in the following nuclear reaction:

$$_{1}H^{2} + _{1}H^{2} \longrightarrow _{2}He^{3} + _{0}n^{1}$$

Assume that the masses of $_1H^2$, $_2He^3$, and neutron (n), respectively, are 2.0141, 3.0160, and 1.0087 in amu.

Sol.
$$\Delta m = [2 \times 2.0141] - 3.0160 - 1.0087 = 3.5 \times 10^{-3} \text{ amu}$$

 $\therefore \Delta E = \Delta m \times 931.478 \text{ MeV}$
 $= 3.5 \times 10^{-3} \times 931.478 = 3.260 \text{ MeV}$
 $\therefore \Delta E = 5.223 \times 10^{-13} \text{ J}$

ILLUSTRATION 6.101

Calculate the binding energy for $_1H^2$ atom. The mass of $_1H^2$ atom is 2.014102 amu where 1n and 1p have their weights 2.016490 amu. Neglect mass of electron.

Sol. Mass of neutron and proton in
$$_1H^2 = 2.016490$$
 amu Actual mass of $_1H^2 = 2.014102$ amu

∴ (
$$\Delta m$$
) Mass defect = 2.388 × 10⁻³ amu
(2.016490 – 2.014102) amu

:. Binding energy =
$$2.388 \times 10^{-3} \times 931.478 \text{ MeV}$$

= 2.2243 MeV

ILLUSTRATION 6.102

The atomic mass of $_8\mathrm{O}^{16}=15.9949$ amu. Calculate the BE/nucleon for this atom. Mass of 1n and 1p is 2.016490 amu and $m_e=0.00055$ amu.

Sol. Mass of
$$\ln + 1p = 2.016490$$
 amu

:. Mass of
$$8n + 8p = 8 \times (2.016490)$$
 amu

:. Total mass of O¹⁶ atom =
$$m(p + n) + m$$
(electron)
= $8 \times (2.016490) + 0.00055 \times 8$
= 16.13632 amu

$$\therefore$$
 Mass defect = $16.1363 - 15.9949 = 0.1414$ amu

∴ BE/nucleon =
$$\frac{\text{Total BE}}{\text{Number of nucleons}} = \frac{131.71}{16}$$

= 8.232 MeV

ILLUSTRATION 6.103

Calculate the mass defect and binding energy per nucleon for an alpha particle whose mass is 4.0028 amu. The mass of protons $(m_p) = 1.0073$ and mass of neutron $(m_p) = 1.0087$ amu.

Sol. An α-particle (₂He⁴) has 2 protons and 2 neutrons.

∴ Mass of
$$2P + 2N$$
 in α -particle
= $2 \times 1.0073 + 2 \times 1.0087$
= 4.032 amu

Mass of α -particle (given) = 4.0028 amu

:. Mass defect
$$(\Delta m) = 4.032 - 4.0028 = 0.0292$$
 amu

Using Einstein equation,
$$E = mc^2 = m \times 931.47 \text{ MeV}$$

$$\therefore \text{ Binding energy per nucleon} = \frac{27.1991}{4}$$
= 6.7997 MeV

ILLUSTRATION 6.104

U-235 is decayed by bombardment by neutron as according to the equation:

$$_{92}U^{235} + _{0}n^{1} \longrightarrow {}_{42}Mo^{98} + _{54}Xe^{136} + x_{-1}e^{0} + y_{0}n^{1}$$

Calculate the value of x and y and the energy released per uranium atom fragmented (neglect the mass of electron).

Given masses (amu) U-235 =
$$235.044$$
,

Xe = 135.907, Mo = 97.90,
$$e = 5.5 \times 10^{-4}$$
, $n = 1.0086$.

The nuclear reaction is:
$$U^{235} + {}_{0}n^{1} \longrightarrow {}_{42}\text{Mo}^{98} + {}_{54}\text{Xe}^{136} + x_{-1}e^{0} + y_{0}n^{1} \quad ...(i)$$
wing the mass of both sides, we get

⁹² Equating the mass of both sides, we get

Equating the mass of cold states, we expect the equation
$$235 + 1 = 98 + 136 + x \times 0 + y \times 1$$

$$235 + 234 + y$$

$$236 = 234 + y$$

$$236 = 234 = 236 - 234 = 2$$

$$\therefore y = 236 - 234 = 2$$

similarly equating the atomic number of both sides,

we get
$$92+0=42+54+x\times(-1)+y\times0$$

$$92 = 96 - x$$

$$x = 96 - 92 = 4$$

$$_{\text{Mass defect of Eq. (i)}}$$
 = Masses of RHS – Masses of LHS = 236.0526 – 235.8264 = 0.2262 amu

$$\therefore$$
 Energy released = mc^2

or
$$E = m \times 931.48 \text{ MeV}$$

$$= 0.2262 \times 931.48 = 210.7 \text{ MeV}$$

ILLUSTRATION 6.105

A positron and an electron collide and annihilated to emit two gamma photons of same energy. Calculate the wavelengths corresponding to this gamma emission.

$$\int_{0}^{\infty} \int_{0}^{\infty} e^{0} + \int_{0}^{\infty} e^{0} \longrightarrow 2\gamma$$

(photons of same energy)

The mass of two electrons is converted into energy.

The energy produced during emission of two photons

$$= 2 \times m_e \times c^2$$

$$= 2 \times m_e \times C^-$$

$$= 2 \times 9.108 \times 10^{-31} \times (3.0 \times 10^8)^2 = 163.9 \times 10^{-15} \text{ J}$$

Energy produced per photon

$$= \frac{16.39 \times 10^{-14} \,\mathrm{J}}{2} = 8.195 \times 10^{-14} \,\mathrm{J}$$

Using Einstein equation,

$$E = \frac{hc}{\lambda}$$
, where $c = \text{velocity of light}$, $\lambda = \text{wavelength of particle}$

$$\therefore 8.195 \times 10^{-14} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{\lambda}$$

$$\therefore \lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{8.195 \times 10^{-14}} = 2.425 \times 10^{-12} \text{ m}$$

$$\lambda = 2.425 \text{ pm}$$

ILLUSTRATION 6.106

The isotopic masses of 1H2 and 2He4 are 2.0141 and 4.0026 amu, respectively. Calculate the quantity of energy liberated when when two moles of 1H² undergo fission to form 1 mol of 2He⁴.

The year The velocity of light in vacuum is 3.0×10^8 m s⁻¹.

$$_{1}H^{2} + _{1}H^{2} \longrightarrow _{2}H^{4} + \text{Energy}$$

Mass defect = 2 × Mass of $_{1}H^{2} - \text{Mass of }_{2}H^{4}$

$$= 2 \times 2.0141 - 4.0026 = 0.0256$$
 amu

Energy released for fusion of two atoms

$$= \Delta mc^2$$

$$= 0.0256 \times 1.66 \times 10^{-27} \times (3.0 \times 10^8)^2$$

$$= 3.8 \times 10^{-12} \text{ J}$$
 [1 amu = 1.66 × 10⁻²⁷ kg]

Energy released per mol of ₂He⁴

$$= 3.8 \times 10^{-12} \times 6.023 \times 10^{23}$$

$$= 2.3 \times 10^{12} \,\mathrm{J}$$

ILLUSTRATION 6.107

Why do radioactive elements decay?

Sol. The stable nuclei are found to have neutron /proton (n/p)ratio in the range 1 to 1.5. The nuclei whose n/p ratio lies outside this range (i.e., <1 or >1.5) lose α - or β -particles so that their n/p ratio shifts into the stability belt.

ILLUSTRATION 6.108

How can a nucleus lose electrons (β -particles) even though free electrons are not present in it?

Sol. A neutron in the nucleus changes to a proton and electron.

ILLUSTRATION 6,109

Balance the following nuclear reactions:

a.
$$_{3}\text{Li}^{7} + _{0}n^{1} \longrightarrow 2_{2}\text{He}^{4} + ?$$

b.
$${}_{42}\text{Mo}^{94} + {}_{1}\text{H}^2 \longrightarrow {}_{0}n^1 + ?$$

Sol.

a. On LHS of the equation

Sum of atomic numbers =
$$3 + 0 = 3$$

Sum of mass numbers =
$$7 + 1 = 8$$

On RHS of the equation,

Let the missing particle be ₇X^a

Sum of atomic numbers = Z + 4

Sum of mass numbers = a + 8

Sum of atomic numbers of LHS

= Sum of atomic numbers of RHS

$$3 = Z + 4$$

or
$$Z = -1$$

Sum of mass numbers of LHS

= Sum of mass numbers of RHS

$$8 = a + 8$$

$$So_{\alpha} = 0$$

Thus, the missing particle is ${}_{1}X^{0}$, i.e., ${}_{1}e^{0}$.

The balanced equation is

$$_{3}\text{Li}^{7} + _{0}n^{1} \longrightarrow 2_{2}\text{He}^{4} + _{-1}e^{0}$$

- **b.** Let the missing particle be ${}_{Z}X^{a}$.
 - On LHS of the equation,

Sum of atomic numbers =
$$(42 + 1) = 43$$

Sum of mass numbers =
$$(94 + 1) = 4$$

On RHS of the equation,

Sum of atomic numbers = Z + 0

Sum of mass numbers = a + 1

ILLUSTRATION 6.110

A sample of uranium mineral was found to contain Pb²⁰⁸ and U²³⁸ in the ratio of 0.008: 1. Estimate the age of the mineral (half life of U^{238} is 4.51×10^9 years).

Sol. Given $t_{1/2}$ of $U^{238} = 4.51 \times 10^9$ years

Ratio by mass of Pb^{206} : $U^{238} = 0.008$: 1

:. Ratio by moles of Pb²⁰⁶: $U^{238} = \frac{0.008}{206}$: $\frac{1}{238} = 0.0092$

We know that

$$K = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \left(\frac{U^{238} + Pb^{206}}{U^{238}} \right) \qquad \left[k = \frac{0.693}{t_{1/2}} \right]$$

$$k = \frac{0.693}{t_{1/2}}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \left(1 + \frac{\text{Pb}^{206}}{\text{U}^{238}} \right)$$

Substituting all values.

$$\frac{0.693}{4.51 \times 10^9} = \frac{2.303}{t} \log (1 + 0.0092)$$

$$\therefore t = \frac{2.303 \times 4.51 \times 10^9}{0.693} \log (1.0092)$$

$$= 0.05945 \times 10^9 \text{ years}$$

$$= 5.945 \times 10^7 \text{ years}$$

ILLUSTRATION 6.111

Which of the following has magic number of protons and neutrons?

b.
$$_{2}\text{He}^{3}$$
 c. $_{50}\text{Sn}^{120}$

Sol. a. 208 and 82 both are magic numbers.

ILLUSTRATION 6.112

A light nuclide that has n/p ratio 2 and has magic number of neutrons but still shows radioactivity

b.
$$_{1}H^{3}$$

c.
$$_{1}H^{2}$$

d.
$$_2$$
He³

Sol. b. For $_{1}H^{3}$, p=1, n=3-1=2

$$\therefore \frac{n}{p} = \frac{2}{1} = 2$$

ILLUSTRATION 6.113

A barn is a unit in nuclear chemistry. One barn is

a. 10^{-24} cm² **b.** 10^{-3} cm² **c.** 10^{-26} cm² **d.** 10^{-6} cm²

b.
$$10^{-3}$$
 cm²

Sol. a. 1 barn = 10^{-24} cm²

ILLUSTRATION 6.114

 $_{15}P^{29}$ has n/p ratio too low for stability. Its stability can be

a. Positron emission

b. Beta-decay

c. Alpha-decay

d. Electron capture

Sol. a. Positron emission increases the number of neutron.

ILLUSTRATION 6.115

Efficiency of nuclear fusion as compared to nuclear fission is

a. More

b. Less

c. Same

d. None is correct

Sol a. In nuclear fusion more energy is released with per gram of fuel.

ILLUSTRATION 6.116

What is enriched uranium?

a. U-238

b. U-235

c. U-235 + Radium

d. U-235 + U-238

Sol. d.

ILLUSTRATION 6.117

In a hydrogen bomb, hydrogen is converted into

a. Barium

b. Uraniun-235

c. Uranium-238

d. Helium

Sol. d. In hydrogen bomb fusion takes place.

ILLUSTRATION 6.118

Which one of the following nuclear transformation is (np) type?

$$a._3Li^7 + _1H^1 \longrightarrow _4Be^7 + _0n^1$$

b.
$$_{33}$$
As⁷⁵ + $_2$ He⁴ $\longrightarrow _{35}$ Bi⁷⁸ + $_0$ n¹

c.
$$_{83}\text{Bi}^{209} + _{1}\text{H}^{2} \longrightarrow _{84}\text{Po}^{210} + _{0}n^{1}$$

d.
$${}_{21}\text{Sc}^{45} + {}_{0}n^{1} \longrightarrow {}_{20}\text{Ca}^{45} + {}_{1}\text{H}^{1}$$

Sol. d. In reaction

$${}_{21}\text{Sc}^{45} + {}_{0}n^{1} \longrightarrow {}_{20}\text{Ca}^{45} + {}_{1}\text{H}^{1}$$

Neutron is attacking while proton is produced along with the product.

ILLUSTRATION 6.119

Insert the missing figure in the following $_{25}\mathrm{Mn}^{55}$ (n,γ) \longrightarrow **a.** $_{25}$ Mn⁵⁶ **b.** $_{24}$ Cr⁵⁶ **c.** $_{24}$ Mn⁵⁶ **d.** $_{24}$ Cr⁵⁶

Sol. a.
$$_{25}\text{Mn}^{55} + _{0}n^{1} \longrightarrow _{25}\text{Mn}^{56} + \gamma$$

ILLUSTRATION 6.120

Write the equations for the following transformations.

a.
$$_{10}$$
K³⁹ (p, d)

b.
$$_{7}N^{14}(n,p)$$

c.
$$_{11}$$
Na²³ (α , p)

d.
$$_{4}\mathrm{Be}^{9}\left(\alpha,n\right)$$

$_{a. 19}K^{39} + _{1}H^{1} \longrightarrow _{19}K^{38} + _{1}H^{2}$

$$\begin{array}{ccc}
\mathbf{a.} & 10^{12} \\
\mathbf{b.} & 7N^{14} + 0N^{1} & \longrightarrow 6C^{14} + 1H^{1}
\end{array}$$

$$b \cdot \tau^{14}$$
 0 $c \cdot 11 Na^{23} + {}_{2}He^{4} \longrightarrow {}_{12}Mg^{26} + {}_{1}H^{1}$

$$\frac{\text{c. }_{11}}{\text{d. }_4\text{Be}^9 + _2\text{He}^4} \longrightarrow {}_6\text{C}^{12} + {}_0n^1$$

ILLUSTRATION 6.121

Which one of the following is an artificial fuel for nuclear

b.
$$Pu^{239}$$
 c. U^{235}

Sol. b. Pu²³⁹

ILLUSTRATION 6.122

Liquid sodium is used in nuclear reactor. What is its function?

Liquid sodium acts as heat exchanger.

ILLUSTRATION 6.123

Which of the following notations shows the product incorrectly?

a.
$$_{96}$$
Cm²⁴² (α , 2 n) $_{97}$ Bl

a.
$$_{95}$$
Cm²⁴² (α , 2 n) $_{97}$ Bk²⁴³ **b.** $_{5}$ B¹⁰ (α , n) $_{7}$ N¹³

c.
$$_{7}N^{14}(n,p)_{6}C^{14}$$

d.
$$_{14}\mathrm{Si}^{28}(d,n)$$
 $_{15}\mathrm{P}^{29}$

📶 a. Equation is not balanced in term of atomic mass number as well as atomic number.

ILLUSTRATION 6.124

Representation of following nuclear reactions are as shown

$$_{7}^{\text{N}^{14}} + _{2}\alpha^{4} \longrightarrow {_{8}}^{\text{O}^{17}} + _{1}p^{1} ; \{_{7}^{\text{N}^{14}} (\alpha, p)_{8}^{\text{O}^{17}} \}$$

$$_{13}$$
Al²⁷ + $_{2}$ α^{4} \longrightarrow $_{15}$ P³⁰ + $_{0}$ n^{1} ; { $_{13}$ A²⁷ (α , n) $_{15}$ P³⁰}

Write the missing particles in representation given below. $_{13}$ Al²⁷, $_{8}$ O¹⁷(--); $_{7}$ N¹⁴, $_{15}$ P³⁰. Also write the corresponding nuclear reaction.

The given reaction is

$$_{7}^{N^{14}} + _{2}\alpha^{4} \longrightarrow {_{8}O^{17}} + _{1}P^{1}; \{_{7}N^{14}(\alpha, p)_{8}O^{17}\}$$
 ...(i)

or
$$_8O^{17} + _1P^1 \longrightarrow {}_7N^{14} + {}_2\alpha^4 \; ; \; \{ _8O^{17} \left(p, \, \alpha \right) \, _7N^{14} \} \; ...(ii)$$

and
$$_{13}Al^{27} + _2\alpha^4 \longrightarrow _{15}P^{30} + _0n^1$$
; $\{_{13}Al^{27} (\alpha, n)_{15}P^{30}\}$...(iii)

On adding Eqs. (ii) and (iii), we get

$$_{13}\text{Al}^{27} + {_8}\text{O}^{17} + {_1}p^1 \longrightarrow {_{15}}\text{P}^{30} + {_7}\text{N}^{14} + {_0}n^1$$

and it can be represented as

$${}_{13}Al^{27}, {}_{8}O^{17}(p, n) {}_{15}P^{30}, {}_{7}N^{14}$$

So, missing particles in representation are p and n.

CONCEPT APPLICATION EXERCISE 6.4

- 1. How does artificial transmutation differ from artificial radioactivity?
- 2. What kind of elementary particles are used in artificial transmutation of elements?
- 3. In a neutron-induced fission reaction of $_{92}\mathrm{U}^{235}$, one of the products is 36Kr95. In this mode another nuclide and three neutrons are also produced. Identify the other nuclide?
- 4. What disadvantages do protons and α -particles have as nuclear projectiles?
- 5. What advantages do protons have over α -particles as nuclear projectiles?
- 6. Why are neutrons superior to protons and α -particles as nuclear projectiles?
- 7. Which isotope of uranium is used in nuclear reactor?
- 8. Name the following processes:

a.
$$_{13}Al^{27} + _{2}He^{4} \longrightarrow _{15}P^{30} + _{0}n^{1} \longrightarrow _{14}Si^{30} + _{1}e^{0}$$

b.
$$_{5}B^{10} + _{2}He^{4} \longrightarrow _{7}N^{13} + _{0}n^{1} \longrightarrow _{6}C^{13} + _{1}e^{0}$$
.

c.
$${}_{5}B^{10} + {}_{2}He^{4} \longrightarrow {}_{6}C^{13} + {}_{1}e^{0}$$

9. Complete the following nuclear reactions:

$$a_{11}Na^{23} + ... \longrightarrow {}_{12}Mg^{23} + {}_{0}n^{1}$$

b.
$${}_{6}C^{12} + ... \longrightarrow {}_{5}B^{10} + {}_{2}He^{4}$$

c.
$$_{13}Al^{27} + ... \longrightarrow {}_{12}Mg^{27} + {}_{1}H^{1}$$

d.
$$_{7}N^{14} + ... \longrightarrow {_{8}O^{17}} + {_{1}H^{1}}$$

e.
$$_{7}N^{14} + ... \longrightarrow {}_{6}C^{11} + {}_{2}H^{4}$$

f.
$$_{13}\text{Al}^{27} + ... \longrightarrow {}_{15}\text{P}^{30} + {}_{0}n^{1}$$

g. $_{17}\text{Cl}^{37} + ... \longrightarrow {}_{18}\text{Ar}^{38} + {}_{0}n^{1}$

h.
$${}_{4}\text{Be}^{9} + {}_{2}\text{He}^{4} \longrightarrow {}_{6}\text{C}^{12} + \dots$$

i.
$$_{92}U^{235} + _{0}n^{1} \longrightarrow _{56}Ba^{141} + _{36}Kr^{92} + ...$$

j.
$$_{13}\text{Al}^{27} + _{2}\text{He}^{4} \longrightarrow _{14}\text{Si}^{30} + ...$$

k.
$$_{6}C^{12} + _{1}H^{2} \longrightarrow {}_{5}B^{10} + ...$$

1.
$$_{92}U^{239} \longrightarrow _{93}Np^{239} + ...$$

10. Complete the following nuclear reactions:

a.
$$_{7}N^{14}(\alpha,...)_{8}O^{17}$$

b
$$_{13}\text{Al}^{27}(\alpha, n) ...$$

c.
$$_{42}^{13}$$
Mo⁹⁶ (... n) $_{43}$ Tc⁹⁷

d. ...
$$(\alpha, 2n)_{85}$$
At²¹¹

e.
$$_{25}$$
Mn⁵⁵ (n, γ) ...

11. Write equations for the following transformations:

a.
$$_{7}N^{14}(n,p)$$

b.
$$_{19}K^{39}(p,\alpha)$$

- 12. A radioactive element absorbs neutron and consequently splits into $_{56}\mathrm{Ba^{140}}$ and $_{36}\mathrm{Kr^{93}}$. Determine the number of neutrons emitted with the help of nuclear reaction.
- 13. 98Cf²⁴⁶ was emmitted along with a neutron when an unknown radioactive substance was bombarded using 6C12 as projectile. Predict the unknown radioactive substance.

- 14. Write nuclear equations for the following tranformations:
 - a. ₈₅At²¹⁸ undergoes α-decay
 - **b.** $_{23}$ Th 233 undergoes β -decay.
- 15. Complete the nuclear reaction ${}_{3}\text{Li}^{7}(\alpha, ...) {}_{3}\text{Li}^{8}$.
- **16.** In a neutron-induced fission reaction of ₉₂U²³⁵, one of the products is ₃₇Rb⁹⁵. In this mode, another nuclide and three neutrons are also produced. Identify the other nuclide.
- 17. What is the main difference between a natural radioactive element and an artificially produced radioactive element?
- 18. The particles more eminent for nuclear fission are
 - a. fast neutrons
- **b.** Slow neutrons
- c. Fast protons
- d. Slow protons

ANSWERS

- 3. ₅₆Ba¹³⁸
- 7. U-235
- **8. a.** Induced radioactivity **b.** Induced radioactivity **c.** Artificial transmutation
- 9. **a.** ₁H¹ **b.** ₁D² **c.** ₀n¹ **d.** ₂He⁴ **e.** ₁H¹ **f.** ₂He⁴ **g.** ₁H²
 - **h.** $_{0}n^{1}$ **i.** 3 $_{0}n^{1}$ **j.** $_{1}$ H¹ **k.** $_{2}$ He⁴ **l.** $_{-1}e^{0}$ (β-particle)
- **10. a. p b.** $_{15}P^{30}$ **c.** H_1^2 **d.** $_{83}Bi^{209}$ **e.** $_{25}Mn^{56}$
- 12. 3 neutrons
- 13. $_{92}U^{235}$ 15. c. $_{2}He^{3}$
- **16.** ₅₅Cs¹³⁸
- 18. a.

6.17 APPLICATIONS OF RADIOACTIVITY AND RADIOISOTOPES

Radioisotopes find numerous uses in different areas such as medicine, chemistry, biology, archeology, agriculture industry, and engineering. Some of the important applications of radioisotopes are as follows:

- a. Discovery of elements: When the phenomenon of radioactivity was discovered, only a few elements such as uranium, polonium, radium, etc., were found to be radioactive. However, the phenomenon of artificial transmutation led to the discovery of a large number of new elements which are also radioactive. The transuranium elements (elements with atomic number 93–105) were first prepared by such transmutation experiments.
- b. Discovery of isotopes and isobars: The emission of α- and β-particles from the natural radioactive elements led to the discovery of isotopes and isobars (as already discussed). It was soon found that the existence of isotopes and isobars, though discovered first in the natural radioactive elements, was not confined to these elements. In fact, at present almost all elements have been found to be isotopic. This has also given the justification for fractional atomic weights.
- c. Activation analysis: The adsorption of neutron by any nucleus produces an activated or energy-rich species that decays by a process characteristic of the nucleus involved. The various isotopes of elements differ considerably in

their ability to absorb neutron. By irradiating a mixture of nuclei with neutrons to saturation limit, it is possible to selectively activate certain elements, detect their presence, and measure their concentration by measuring the intensity of the induced radioactivity. The sensitivity of the neutron activation analysis depends on the neutron flux available for irradiation, the availability of nucleus to absorb a neutron, and the energy of the decay process. This method is very useful for the determination of elements present in trace quantities. For example, it is possible to detect as little as 10^{-40} g of copper or tungsten by activation analysis.

d. Tracers: By incorporating a small amount of radioisotope in a reaction system, one can trace the course of the reaction. Such a sample of radioisotope is called tracer. Since all the isotopes of an element are chemically equivalent, the monitored path of the isotope will indicate the path of the reaction. For example, consider the problem of determining the course of esterification such as:

$$C_6H_5C \nearrow O + CH_3OH \longrightarrow C_6H_5C \nearrow O + H_2O$$

Does the starred oxygen come from alcohol or from the acid? By labelling the oxygen atom of methanol with O¹⁸ and then using it in the esterification, it can be proved that the starred oxygen come from the alcohol and not from the acid as the ester is found enriched with ¹⁸O isotope. Many other mechanistic applications have been reported. The use of ¹⁴C as a radioactive tracer using labelled compounds is well known. The dynamic nature of chemical equilibria has been established by the use of labelled compounds.

For example, in studying the mechanisms and rate of certain reactions such as, the transformation of N-chloroacetanilide into *p*-chloroacetanilide takes place in the presence of hydrochloric acid as follows:

$$Cl$$
— N — $COCH_3$ H — N — $COCH_3$ H Cl

To know whether the mechanism of the reaction involves Cl of HCl or not, hydrochloric acid containing radioactive chlorine (represented by HCl*) is used. The two probable mechanisms are:

i.
$$HCl^*$$
 $H-N-COCH_3$
 $+HCl^*$

In which involves only intermolecular rearrangement and Cl of HCl* is not involved.

ii.
$$H-N-COCH_3$$
 $H-N-COCH_3$ $+ HCI$

In which Cl of the HCl* is involved.

In actual experiment, the p-chloroacetanilide formed is found In action to be radioactive. hence reaction proceeds by mechanism (ii) and not by (i).

A compound containing a radioactive element (e.g., HCl* in the above cases) is said to be labelled or tagged. The reactions of the above type involving exchange of an atom by its radioactivity isotope are called exchange reactions. The rate of such reactions can be determined by measuring the radioactivity of the product formed at different intervals of time. Similarly, the fact that the photosynthesis involves CO₂ has been confirmed using labelled *CO₂ containing C-14 isotope—the glucose formed is found to be radioactive.

$$*_{6\text{CO}_2} + 6\text{H}_2\text{O} \xrightarrow{\text{Sunlight}} *\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$

e. Age of minerals and rocks: The determination of age of minerals and rocks is an important part of geological studies. This may involve the determination of either a species formed during a radioactive decay or of the residual activity of an isotope which is undergoing decay.

The former may be illustrated by helium dating. Helium present in uranium mineral has almost certainly been formed from α -particles. A gram of uranium in equilibrium with its decay produces approximately 10^{-7} g of helium per year. So if the helium and uranium contents of a mineral are known, the age of the mineral can be estimated. The latter can be typified by considering a rock containing $_{92}\mathrm{U}^{238}$ which has a half life of 4.5×10^9 years. We have seen that in the uranium decay series, $_{92}\mathrm{U}^{238}$ after a series of decay gives the stable isotope $_{82}\text{Pb}^{206}$ as the end product. Assuming that initially the rock did not contain any lead, we can determine the age of the rock by measuring the ratio of $_{92}\mathrm{U}^{238}$ and $_{82}\mathrm{Pb}^{206}$ and using the equation,

$$N_{\rm t} = N_0 e^{-Kt}$$

where N_0 and N_t are the amounts of uranium present initially (t=0) and after the lapse of time t, respectively, and K is the decay constant. Suppose, the molar ratio of uranium and lead is 1:1, it means half of the uranium originally present has undergone decay, finally giving the lead isotope. The age of the rock in that case will be equal to the half-life period of $_{92}$ U²³⁸ (i.e., 4.5×10^9 years). Most of the rocks contain lead/uranium ratio much less than unity indicating that the age of rocks may be less than the half-life period of $_{92}\mathrm{U}^{238}$. For example: Let a sample of uranium rock is analysed for U-238 and Pb-206 contents. From this analysis, let the quantities in mole be $N = U^{238}$ mole, $N_0 = U^{238}$ mole + Pb²⁰⁶ mole. Applying disintegration equation,

$$\lambda t = 2.303 \log \left(\frac{N_0}{N} \right)$$
$$= 2.303 \log \left(\frac{U^{238} + Pb^{206}}{U^{238}} \right)$$

$$=2.303 \log \left(1 + \frac{Pb^{206}}{U^{238}}\right)$$

The value of t can be calculated by putting the value of λ which is equal to $0.693/t_{1/2}$.

So,
$$t = \frac{2.303 \times t_{1/2}}{0.693} \log \left[1 + \frac{\text{Pb}^{206}}{\text{U}^{238}} \right]$$

Here t corresponds to the age of earth which has been found to be 4.5 billion years.

f. Radiocarbon dating: Radiocarbon $\binom{6}{6}$ C¹⁴) dating of historical wooden-derived objects is based on the knowledge that the cosmic ray intensity (responsible for C^{14} production) has been practically constant for thousands of years. C14 is formed in the upper atmosphere by the action of cosmic radiation on N14,

$$_{7}N^{14} + _{0}n^{1} \longrightarrow {}_{6}C^{14} + _{1}H^{1}$$

The C14 so produced is eventually converted into carbon dioxide, which in turn is incorporated into plants and trees by the process of photosynthesis and then finds way into animals which eat plants. Because of the natural plantanimal cycle, an equilibrium is set up and all living matter contains the same small proportion of C14 as it occurs in the atmosphere. Once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of C14 in the dead begins to fall due to the decay which C14 undergoes.

$$_{6}C^{14} \longrightarrow _{7}N^{14} + \beta^{\odot}$$

The half-life $(t_{1/2})$ period of C^{14} is 5770 years. A comparison of the β^{\odot} -activity of the dead matter with that of the carbon still in circulation enables measurement of the period of isolation of the material from the living cycle. The method, however, ceases to be accurate over periods longer than two or three half-life periods of C^{14} . The proportion of C^{14} to C^{12} in living matter is 1: 10^{12} .

g. In medicine-radiotherapy: One of the first applications of radioactivity was based upon the fact that the radiation (γ -rays) emitted by the radioactive substance ($_{27}\text{Co}^{60}$) destroyed the cells. Hence, it was used in the treatment of cancer in which the malignant cells are wiped out. Similarly, the use of radium in the treatment of cancer is well known. In another applications, male insects have been irradiated to destroy their reproductive cells. For instance, millions of sterilized flies were released near cattle farms where they mated with female flies who then produced no offspring. In this way, the flies which do great damage to live-stock were eliminated in several areas. Similarly, the isotope 57I131 is used in the treatment of goitre, i.e., thyroid disorders (hyperthyroidism) and radiophosphorus ($_{15}P^{32}$) is used in the treatment of leukaemia.

 Y^{20} : This isotope is used in the treatment of joint effusion and arthritis.

Fe⁵⁹: Used in the detection of anaemia. Co⁶⁰: Used in cancerous tumor detection and treatment.

Na²⁴: Used to locate blood clots and circulatory disorder.

As⁷⁴: Used in the detection of presence of tumors.

h. In agriculture: The uses of radioactive phosphorus P³² in fertilizers has revealed how phosphorus is absorbed by plants. This study has led to an improvement in the preparation of fertilizers. C¹⁴ is used to study the kinetics of photosynthesis.

O¹⁸: Used in the study of mechanism of photosynthesis.

i. In industry: Radioisotopes are used in industry to detect the leakage in underground oil pipelines, gas pipelines, and water pipes. Radioactive isotopes are used to measure the thickness of materials, to test the wear and tear inside a car engine, and the effectiveness of various lubricants. Radioactive carbon has been used as a tracer in studying mechanisms involved in many reactions of industrial importance such as alkylation, polymerization, catalytic synthesis, etc.

ILLUSTRATION 6.125

Does hydrogen bomb involve only nuclear fusion? Why or why not?

Sol. Hydrogen bomb involves nuclear fission also in the centre.

This is because fusion can take place only at very high temperatures.

ILLUSTRATION 6.126

What is the role of heavy water in a nuclear reactor?

Sol. It acts both as a moderator and a coolant.

ILLUSTRATION 6.127

How is plutonium obtained?

Sol.
$$_{0}n^{1} + _{92}U^{238} \longrightarrow _{92}U^{239} \xrightarrow{-\beta} _{93}Np^{239} \xrightarrow{-\beta} _{94}Pu^{239}$$

ILLUSTRATION 6.128

What is the source of radioactive CO₂ in the atmosphere?

Sol. ₇N¹⁴ is hit by cosmic ray neutrons to produce ₆C¹⁴ which is radioactive and is oxidized to produce radioactive CO₂.

ILLUSTRATION 6.129

How can the circulation of blood be tested by using radioisotope?

Sol. By injecting a saline solution containing a little radioactive Na-24 isotope and then detecting its presence in different parts using a Geiger-Muller counter.

ILLUSTRATION 6.130

Why a huge amount of energy is released in nuclear fission or nuclear fusion solution? **Sol.** This is because of a large mass defect, i.e., $E = \Delta mc^2$, where $\Delta m =$ mass defect and c = velocity of light.

ILLUSTRATION 6.131

An old piece of wood has 25.6% as much $\rm C^{14}$ as ordinary wood today has. Find the age of the wood. Half-life period of $\rm C^{14}$ is 5760 years.

Sol. Suppose the amount of C^{14} present in the wood originally (i.e., the same which the wood today has) = a.

Then the amount of C14 present now in the old wood

$$(a-x) = \frac{25.6}{100} a = 0.256a$$

The time t in which C^{14} changed from a to 0.256a will then be given by

$$t = \frac{2.303}{K} \log \frac{a}{0.256a}$$
But $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{5760} = 1.203 \times 10^{-4} \text{ year}^{-1}$

$$\therefore t = \frac{2.303}{1.203 \times 10^{-4}} \log \frac{1}{0.256}$$
= 11329 years

ILLUSTRATION 6.132

The $_6\mathrm{C}^{14}$ and $_6\mathrm{C}^{12}$ ratio in a piece of woods is 1/16 part that of atmosphere. Calculate the age of wood. $t_{1/2}$ of C^{14} is 5577 year.

Sol. Given,
$$\frac{N_{C_{14}}}{N_{C_{12}}} = \frac{1}{16} \frac{N_{0C_{14}}}{N_{0C_{12}}}$$

Since, only C¹⁴ undergoes decay.

$$N_{C12} = N_{OC12}$$
or
$$\frac{N_{0C_{14}}}{N_{C_{14}}} = \frac{16}{1}$$

$$t = \frac{2.303}{\lambda} \log \frac{16}{1} = \frac{2.303}{0.693} \times 5577 \log 2^4$$

$$t = 5577 \times 4 = 22308 \text{ year}$$

ILLUSTRATION 6.133

The half-life period of C¹⁴ is 5760 year. A piece of wood when buried in the earth had 1% C¹⁴. Now as charcoal it has only 0.25% C¹⁴. How long has the piece of wood been buried?

Sol.
$$t_{1/2}$$
 of $C^{14} = 5760$ year

$$\lambda = \frac{0.693}{5760} \text{ year}^{-1}$$

$$N_{0C^{14}} = 1\%$$

$$N_{C^{14}} = 0.25\%$$

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

$$= \frac{2.303 \times 5760}{0.693} \log \frac{1}{0.25} = \frac{2.303 \times 5760}{0.693} \log 2^2$$

t = 11520 year

ILLUSTRATION 6.134

Awooden artifact sample gave activity 32 β-particles per second Awould he freshly cut wood gave activity of 64 β-particles per second while the freshly cut wood gave activity of 64 β-particles per second in Geiger Muller counter. Calculate the age of the wooden artifact $(l_{1/2})$ of $C^{14} = 5760$ years)

- a. 11520 years
- **b.** 5760 years
- c. 2880 years
- d. 1440 years

Sol. b. $\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{ace}} \log\left(\frac{N_0}{N}\right)$ $\frac{0.693}{5760} = \frac{2.303}{t_{\text{age}}} \log \left(\frac{64}{32}\right)$

$t_{\rm age} = 5760 \text{ years}$

ILLUSTRATION 6.135

The amount of 6C14 isotope in a piece of wood is found to be one-fifth of that present in a fresh piece of wood. Calculate the age of wood (Half life of $C^{14} = 5577$ years).

Sol. We know that
$$t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{N_0}{N}$$

Given
$$N = \frac{N_0}{5}$$

So $t = \frac{2.303 \times 5577}{0.693} \log 5$
or $t = \frac{2.303 \times 5577}{0.693} \times 0.6989 = 12953 \text{ years}$

ILLUSTRATION 6.136

A piece of wood was found to have C^{14}/C^{12} ratio 0.6 times that in a living plant. Calculate the period when the plant died. (Half life of $C^{14} = 5760$ years.).

Sol. We know that
$$t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{N_0}{N}$$

So
$$t = \frac{2.303 \times 5760}{0.693} \log \frac{1}{0.6}$$

= $\frac{2.303 \times 5760}{0.693} \times 0.2201$
= 4213 years

LLUSTRATION 6.137

Which of the following radioactive isotopes is used for the diagnosis of hyperthyroidism?

- a. Co60
- **b.** P^{32}
- $c. I^{131}$
- **d.** C^{14}

Sol. c.

CONCEPT APPLICATION EXERCISE 6.5

- 1. A sample of ¹⁴CO₂ was to be mixed with ordinary CO₂ for a biological tracer experiment. In order that 10 mL (STP) of the diluted gas should have 10⁴ dpm, how many microcuries of radioactive carbon are needed to prepare 60 L of the diluted gas?
- 2. A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5 × 10⁹ years). What is the age of the rocks?
- 3. Name the process represented below:

a.
$$_{33}$$
As⁷⁵ + $_{1}$ H² $\longrightarrow _{25}$ Mn⁵⁶ + 9_{1} H¹ + 12_{0} n¹

b.
$$_{5}B^{10} + _{2}He^{4} \longrightarrow {}_{7}N^{13} + {}_{0}n^{1} \longrightarrow {}_{6}C^{13} + {}_{+1}e^{0}$$

c.
$${}_{5}B^{10} + {}_{2}He^{4} \longrightarrow {}_{6}C^{13} + {}_{1}H^{1}$$

d.
$$_{13}Al^{27} + _{2}He^{4} \longrightarrow _{15}P^{30} + _{0}n^{1} \longrightarrow _{14}Si^{30} + _{+1}e^{0}$$

4. Calculate the group of elements formed in the final stage of radioactive changes given below:

a.
$$_{92}U^{235} \xrightarrow{-\alpha} _{90}Th^{231}$$
III group

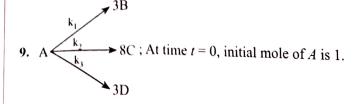
$$\mathbf{b.} \xrightarrow{92} \mathrm{Th}^{231} \xrightarrow{-\beta} \xrightarrow{91} X^{231}$$
III group

$$\begin{array}{ccc} \mathbf{c.} & _{91}\mathbf{X}^{231} & \xrightarrow{-\alpha} & _{89}\mathbf{Ac}^{227} \\ & & \text{III group} \end{array}$$

$$\mathbf{d.} \xrightarrow{90} \text{Th}^{231} \xrightarrow{-\alpha} \underset{88}{\longrightarrow} \text{Ra}^{227}$$
III group

- 5. Atoms ₇A, ₈B, and ₉C¹⁷ are such that ₈B is an isobar of 7 A and atom 9C17 is isotone to 8B. Calculate the mass number for A and B.
- 6. Which one(s) of the following processes alpha emission, beta emission, positron emission, electron capture - cause (a) increase in atomic number, (b) a decrease in atomic number (c) emission of an X-ray in every case?
- 7. i. Classify each one of the following nuclides as "probably stable," "beta emitter," or "position emitter": $_{20}$ Ca⁴⁹, $_{80}$ Hg¹⁹⁵, $_{82}$ Pb²⁰⁸, $_{5}$ B⁸, $_{67}$ Ho¹⁵⁰, $_{13}$ Al³⁰, $_{50}$ Sn¹²⁰,

8. Speculate on the existence of a world composed of negative antioprotons and positrons (along with an array of other antiparticles) and neutrons. Would the chemistry in such a world have formulas similar to those of compounds on earth? What would happen if material from earth encountered material from the "antiworld"?



Overall half life of the reaction is 15 days. Then calculate the number of mole of C after 45 days if the ratio of $k_1 : k_2 : k_3$

10. In the given radioactive disintegration series $_{92}U^{235} \longrightarrow _{92}Pb^{207}$

Calculate difference between number of α and number of β particles emitted in this series.

11. A, B and C are isodiaphers while C, D and E are isobars. Calculate the difference of proton between A and E

$$_{82}A^{206} \longrightarrow B \longrightarrow C \longrightarrow D \longrightarrow E$$

Given: Isodiaphers and isobars are formed in successive α and β -emission respectively.

12. In the given radioactive disintegration series.

$$_{90}$$
Th²³² \longrightarrow $_{82}$ Pb²⁰⁸

Calculate value of (n + 2)

Where value of n is number of isobars formed in this serie, suppose there is successive emission of β -particles.

13. The average life of a radioactive element is 7.2 min. Calculate the time interval (in min.) between the stages of 33.33% and 66.66% decay

ANSWERS

- 1. 27.0 mCi
- **2.** 4.45×10^9 years

Solved Examples

EXAMPLE 6.1

How many α- and β-particles are emitted when an atom of ₉₀Th²³² undergoes disintegration to produce an atom of ₈₂Pb²⁰⁸?

Sol.
$$_{90}\text{Th}^{232} \longrightarrow {}_{82}\text{Pb}^{208} + x_2\text{He}^4 + y_{-1}e^0$$

Remembering that the total atomic number as well as mass number must be equal to the two sides of the equation, we

$$208 + 4x + 0y = 232$$

i.e.,
$$4x = 24$$
 ...(i)

and
$$82 + 2x - y = 90$$

or
$$2x - y = 8$$
 ...(ii)

Solving Eqs. (i) and (ii), we get x = 6 and y = 4.

EXAMPLE 6.2

The actual atomic mass of 20Ca40 is 39.96259 amu. Find the binding energy for this nuclide, using 1.008665 amu for the mass of a neutron and 1.007825 amu for the mass of atomic hydrogen. Also calculate the binding energy per nucleon.

- Sol. Mass of 20Ca⁴⁰ atom
 - = Mass of 20 atoms of hydrogen + Mass of 20 neutrons
 - $= 20 \times 1.007825 + 20 \times 1.008665 = 40.32980$ amu

Actual mass of $_{20}$ Ca⁴⁰ atom = 39.96259 amu (given)

 \therefore Mass defect (ΔM) = 40.32980 - 39.96259

For a mass defect of 0.36721 amu, energy released $= 931.5 \times 0.36721 \text{ MeV} = 342.06 \text{ MeV}$

EXAMPLE 6.3

14 g of a radioactive substance decays to 7 g in 20 min. Will the time required be more or less for the following processes.

- i. 20 g decreases by 8 g
- ii. 20 g decreases to 8 g. Explain.
- Sol. Since 14 g decays to 7 g in 20 min, this means that halflife period $(t_{1/2}) = 20$ min.

In case (i), 20 g decreases by 8 g. This means that less than half of the substance decays. Hence, time taken will be less than 20 min.

In case (ii), 20 g decreases to 8 g. This means 12 g of the substance decays which is more than half of the original substance. Hence, the time taken will be more than 20 min. The exact calculation of times in the two cases can be done as follows:

From the first data

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{20} = 0.03465 \,\mathrm{min}^{-1}$$

$$t = \frac{2.303}{K} \log \frac{a}{a - x} = \frac{2.303}{0.03465} \log \frac{20}{20 - 8} = 14.74 \text{ min}$$

$$t = \frac{2.303}{K} \log \frac{a}{a - x} = \frac{2.303}{0.03465} \log \frac{20}{8} = 26.45 \text{ min}$$

EXAMPLE 6.4

The final product of U²³⁸ is Pb²⁰⁶. A sample of pitchblende contains 0.0453 g of Pb²⁰⁶ for every gram of U²³⁸ present in it. Supposing that the mineral pitchblende formed at the time of formation of the earth did not contain any Pb206, calculate the age of the earth (half-life period of $U^{238} = 4.5 \times 10^9$ years).

Sol. Amount of U²³⁸ now present, i.e., a - x = 1 g

Amount of U²³⁸ originally present

= Amount of U²³⁸ now present + Amount of U²³⁸ changed into 0.0453 g of Pb²⁰⁶

$$= 1 g + \frac{238}{206} \times 0.0453 g = 1.05234 g$$

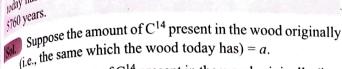
If t is the time in which 1.05234 of U^{238} changed into 1 g of U²³⁸, then

$$t = \frac{2.303}{K} \log \frac{a}{a - x}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9} = 1.54 \times 10^{-10} \text{ year}^{-1}$$

$$2.303 \over 1.54 \times 10^{-10} \log \frac{1.05234}{1} = 3.29 \times 10^8 \text{ years}$$

EXAMPLE 6.5 Moldpiece of wood has 25.6% as much C¹⁴ as ordinary wood Find the age of the wood Half 1:6. An old piece as ordinary wood as ordinary wood has. Find the age of the wood. Half-life period of C¹⁴ is



Then the amount of C^{14} present in the wood originally (i.e., the same which the wood today has) = a. Then the amount of C¹⁴ present now in the old wood

$$=\frac{25.6}{100}a=0.256a$$

The time t in which C^{14} changed from a to 0.256a will then

$$t = \frac{2.303}{K} \log \frac{a}{0.256a}$$

But
$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{5760} = 1.203 \times 10^{-4} \text{ year}^{-1}$$

$$t = \frac{2.303}{1.203 \times 10^{-4}} \log \frac{1}{0.256} = 11329 \text{ years}$$

EXAMPLE 6.6

The half-life of cobalt-60 is 5.26 years. Calculate the percentage activity remaining after 4 years.

$t_{1/2} = 5.26 \text{ years}$

$$K = \frac{0.693}{5.26} \text{ year}^{-1}$$

and
$$t = 4$$
 years

The aim is to find
$$\frac{a-x}{a} \times 100$$

On applying the relationship
$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\frac{0.693}{5.26} = \frac{2.303}{4} \log \frac{a}{a - x}$$

or
$$\log \frac{a}{a-x} = 0.2288$$

or
$$\frac{a}{a-x}$$
 = Antilog 0.2288 = 1.693

or
$$\frac{a-x}{a} = \frac{1}{1.693} = 0.59$$

$$\therefore$$
 % age activity = 0.59 × 100 = 59%

EXAMPLE 6.7

The activity of 1 g of radium is found to be 0.5 curie. Calculate the half-life period of radium and the time required for the decay of 2 g of radium to give 0.25 g of radium (atomic mass

of radium = 226).

Number of atoms in 1 g of
$$Ra^{226} = \frac{6.02 \times 10^{23}}{226}$$

Activity, i.e.,

$$-\frac{dN}{dt} = 0.5 \text{ curie} = 0.5 \times 3.7 \times 10^{10} \text{ dps}$$
$$= 1.85 \times 10^{10} \text{ dps}$$

But
$$-\frac{dN}{dt} = KN$$
, i.e., $1.85 \times 10^{10} = K \times \frac{6.02 \times 10^{23}}{226}$

or
$$K = 6.945 \times 10^{-12} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{6.945 \times 10^{-12}} \text{ s}$$

$$= 9.978 \times 10^{10} \text{ s}$$

$$= \frac{9.978 \times 10^{10}}{3600 \times 24 \times 365} \text{ years} = 3164 \text{ years}$$

Time required for decay of 2 g of Ra to 0.25 g = three halflives = $3 \times 3164 = 9492$ years

EXAMPLE 6.8

It is found that 3.125×10^{-8} g atoms of Rn exist in equilibrium with 1 g of radium at 0°C and 1 atm pressure. The disintegration constant of Ra is 1.48×10^{-11} s⁻¹. Calculate the disintegration constant of Rn.

Sol. Number of g atoms of Ra²²⁶ in 1 g of Ra²²⁶

$$= 1/226 = 4.425 \times 10^{-3}$$

At equilibrium
$$K_A N_A = K_B N_B$$

$$K_{Rn} \times N_{Rn} = K_{Ra} \times N_{Ra}$$

or
$$\frac{K_{\rm Rn}}{K_{\rm Ra}} = \frac{N_{\rm Ra}}{N_{\rm Rn}}$$

$$K_{Rn} = \frac{N_{Ra}}{N_{Rn}} \times K_{Ra}$$

$$= \frac{4.425 \times 10^{-3}}{3.125 \times 10^{-8}} \times 1.48 \times 10^{-11} \text{ s}^{-1}$$

$$= 2.095 \times 10^{-6} \text{ s}^{-1}$$

EXAMPLE 6.9

What mass of C^{14} with $t_{1/2} = 5730$ years has activity equal to curie?

Sol. 1 curie =
$$3.7 \times 10^{10}$$
 dps

i.e., rate =
$$3.7 \times 10^{10} \, dps$$

Now Rate = $K \times Number of atoms$

$$3.7 \times 10^{10} = \frac{0.693}{5730 \times 365 \times 24 \times 60 \times 60} \times \text{Number of atoms}$$

$$\therefore \text{ Number of atoms} = 9.65 \times 10^{21}$$

Now
$$6.023 \times 10^{23}$$
 atoms of $C^{14} = 14$ g

$$\therefore 9.65 \times 10^{21} \text{ of } C^{14} = \frac{14 \times 9.65 \times 10^{21}}{6.023 \times 10^{23}} = 0.2243 \text{ g}$$

EXAMPLE 6.10

The disintegration rate of a certain radioactive sample at any instant is 4750 dpm which becomes 2700 dpm 5 min later. Calculate the half life of sample.

Sol.
$$r_0 = 4750 \text{ dpm}$$

$$r_1 = 2700 \text{ dpm}$$
 at $t = 5 \text{ min}$

$$\therefore \frac{r_0}{r_0} = \frac{4750}{2700}$$

$$\therefore \frac{r_0}{r_l} = \frac{N_0}{N_t} = \frac{4750}{2700}$$

$$\therefore t = \frac{2.303}{K} \log \frac{N_0}{N_t}$$

$$5 = \frac{2.303}{K} \log \frac{4750}{2700} \text{ or } K = 0.113 \text{ min}^{-1}$$

$$\therefore t_{1/2} = \frac{0.693}{0.113} = 6.13 \,\text{min}$$

EXAMPLE 6.11

A radioisotope $_ZA^m$ ($t_{1/2} = 10$ days) decays to give $_{Z-6}B^{m-12}$ stable atom along with α -particles. If m g of A are taken and kept in a sealed tube, how much He will accumulate in 20 days at STP>

Sol.
$$Z^{A^m \longrightarrow Z-6} B^{m-12} + 3_2 He^4$$

Given weight of A = m g

$$\therefore$$
 Moles of A (No) = 1 g mol

Also
$$t = 20$$
 days; $t_{1/2} = 10$ days

$$\therefore n=2 \ (t=t_{1/2}\times n)$$

$$\therefore$$
 Amount left in 2 halves = $\frac{1}{2^2}$ mol = $\frac{1}{4}$ mol

∴ Amount decayed in 2 halves =
$$1 - \frac{1}{4} = \frac{3}{4}$$
 mol

$$\therefore$$
 Amount of He formed = $3 \times \frac{3}{4} \text{ mol} = \frac{9}{4} \text{ mol}$

(decay of 1 mol gives 3 mol of He)

$$\therefore \text{ Volume of He STP} = \frac{22.4 \times 9}{4} = 50.4 \text{ L}$$

EXAMPLE 6.12

At radioactive equilibrium, the ratio between two atoms of radioactive elements A and B is 3.1×10^9 : 1. If the half-life period of A is 2×10^{10} years, what is the half life of B?

Sol. At radioactive equilibrium A — → B

$$\frac{N_{\rm A}}{N_{\rm B}} = \frac{K_{\rm B}}{K_{\rm A}} = \frac{t_{1/2\,\rm A}}{t_{1/2\,\rm B}}$$

$$\therefore \frac{3.1 \times 10^9}{1} = \frac{2 \times 10^{10}}{t_{1/2B}} \text{ and } t_{1/2B} = 6.45 \text{ years}$$

EXAMPLE 6.13

The mean lives of a radioactive substance are 1620 years and 405 years of α -emission and β -emission, respectively. Find out the time during which three-fourth of a sample will decay if it is decaying both by α -emission and β -emission simultaneously.

Sol. For successive α - and β -emission

$$K_{\text{avg}} = K_{\alpha} + K_{\beta} = \frac{1}{1620} + \frac{1}{405} = \frac{5}{1620} \text{ year}^{-1}$$

Given at t = t;

 $N = 1/4N_0$ (since 3/4 part decays)

$$t = \frac{2.303}{K_{\text{avg}}} \log \frac{N_0}{N}$$

$$= \frac{2.303 \times 1620}{5} \log 4 = 449.24 \text{ years}$$

EXAMPLE 6.14

Calculate the effective neutron capture radius of a nucleus having a cross section of 1.0 barn.

Sol. $1.0 \text{ barn} = 1.0 \times 10^{-24} \text{ cm}^2 = 10^{-28} \text{ m}^2$

The area of a circle is given by $A = \pi r^2$

Hence,
$$r = \sqrt{A/\pi}$$

= $\sqrt{(1.0 \times 10^{-24} \text{ cm}^2)/3.14}$
= $5.6 \times 10^{-13} \text{ cm}$

EXAMPLE 6.15

A 0.20 mL sample of a solution containing 1.0×10^{-7} Ci of $_1$ H³ is injected into the blood stream of a laboratory animal. After sufficient time of a circulatory equilibrium to be established, 0.10 mL of blood is found to have an activity of 20 dpm. Calculate the blood volume of the animal.

Sol. In the injected sample the activity is

$$(1.0 \times 10^{-7} \text{ Ci}) \left(\frac{3.7 \times 10^{10} \text{ dps}}{\text{Ci}} \right) = 3.7 \times 10^{3} \text{ dps}$$

In the sample withdrawn = (20 dpm) (1 min/60 s)= 0.33 dps

The total activity of the entire blood volume is equal to the activity of the sample injected. The ratio of total activity of sample withdrawn is equal to the ratio of volumes, where V is the original body blood volume:

$$\frac{3.7 \times 10^3 \text{ dps}}{0.33 \text{ dps}} = \frac{V + 0.20 \text{ mL}}{0.10 \text{ mL}}$$

$$V = 1.1 \times 10^3 \text{ mL} = 1.1 \text{ L}$$

EXAMPLE 6.16

A sample of $_{53}I^{131}$, as iodide ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? Of what diagnostic value is such an experiment? ($t_{1/2} = 8$ days)

Sol.
$$K = \frac{2.303}{t} \log \frac{N_0}{N_t}$$
 $\left(K = \frac{0.693}{t_{1/2}}\right)$

$$0.693 = \frac{2.303}{4} \log \frac{N_0}{N_t}$$

$$\frac{N_0}{N_0} = 1.414$$

$$\frac{0.693}{8} = \frac{1.414}{4} \quad \text{or} \quad \frac{N_t}{N_0} = 0.707 = 70.7\%$$

$$\frac{N_0}{N_t} = 1.414 \quad \text{or} \quad \frac{N_t}{N_0} = 0.707 = 70.7\%$$

practical % left in thyroid gland = 67.7%

Theoretical % left of the initial conc = 70.7%

Theoretical % left of the introduction of the piagnostic value =
$$\frac{67.7}{70.7} \times 100 = 95.8\%$$

Amount left =
$$\left(\frac{1}{2}\right)^{1/2} \times a_0$$

$$= 0.707 \times 0.1 \text{ mg}$$

= 0.0707 mg of
$$I^{\odot}$$

Amount decomposed of $I^{\odot} = 0.1 - 0.0707$ = 0.029 mg

Diagnostic value =
$$\frac{0.029 \times 95.8}{100}$$
 = 0.02778 mg

EXAMPLE 6.17

mg of Th emits 22 α -particles per unit solid angle per minute. Calculate $t_{1/2}$ of Th (Th = 232).

Numbers of α -particles per minute in all directions emitted $=22 \times 4\pi = \frac{22 \times 4\pi}{60} \text{ s}^{-1}$

Number of atoms in 1 mg of Th = $\frac{10^{-3} \text{g} \times 6.02 \times 10^{23}}{232}$

Decay per second = $\frac{22}{15}\pi$

$$\therefore \frac{22}{15}\pi = \frac{K \times 10^{-3} \times 6.02 \times 10^{23}}{232}$$

$$\therefore K = 1.77 \times 10^{-18}$$

and
$$t_{1/2} = \frac{0.693}{K} = 1.238 \times 10^{10}$$
 years

EXAMPLE 6.18

A solution contains 1 mCi of L-phenylalanine C14 labelled in 2.0 mL solution. The specific activity of labelled sample is given as 150 mCi mmol-1. Calculate

- a. The concentration of the sample in the solution in $mol L^{-1}$.
- b. The activity of solution in terms of counting per minute per mL at counting efficiency of 80%.

Sol.

a. 1 mmol =
$$150 \text{ mCi}$$
,

1 mCi =
$$\frac{1}{150}$$
 mmol = $\frac{1}{150 \times 2}$ = 3.33×10⁻² M

b. 1 Ci =
$$3.7 \times 10^{10}$$
 dps

$$= 3.7 \times 10^{10} \times 60 \text{ dpm}$$

$$= 3.7 \times 10^{10} \times 60 \times \frac{80}{100} \text{ counts min}^{-1}$$

$$= \frac{177.6 \times 10^{10}}{2 \text{mL}} = 88.8 \times 10^{10} \text{ counts min}^{-1} \text{ mL}^{-1}$$

$$1 \text{ mCi} = 88.8 \times 10^7 \text{ counts min}^{-1} \text{ mL}^{-1}$$

Exercises

Single Correct Answer Type

Radioactivity and Group Displacement Law

- 1. An element X loses one α and two β -particles in three successive stages. The resulting element will be
 - (1) An isobar of X
- (2) An isotope of X
- (3) X itself
- (4) An isotone of X
- 2. Which of the following detects radiations by flashes produced on a phosphor screen?
 - (1) GM counter
- (2) Bubble chamber
- (3) Ionization chamber
- (4) Scintillation counter
- 3. Decrease in atomic number is observed during
 - (1) Alpha emission
- (2) Beta emission
- (3) Positron emission
- (4) Electron emission
- 4. Particles having energy of several hundred MeV are known
 - (1) Electrons
- (2) Nucleons
- (3) Fast particles
- (4) Super fast particles
- 5. The triad of nuclei that is isotonic is
 - $(1)_{6}C^{14}$, $_{7}N^{15}$, $_{9}F^{17}$
- $(2)_{6}C^{12}$, $_{7}N^{14}$, $_{9}F^{19}$
- $(3)_{6}C^{14}$, $_{7}N^{14}$, $_{9}F^{17}$
- $(4)_{6}C^{14}$, $_{7}N^{14}$, $_{9}F^{19}$
- 6. Natural radioactivity was discovered by
 - (1) Schmidt
- (2) Curie
- (3) Becquerel
- (4) Rutherford
- 7. Radioactivity is due to
 - (1) Stable electronic configuration
 - (2) Unstable electronic configuration
 - (3) Stable nucleus
 - (4) Unstable nucleus
- 8. Radium is a radioactive substance. It dissolves in dilute H₂SO₄ and forms a compound radium sulphate. The compound is
 - (1) No longer radioactive
 - (2) Half as radioactive as the radium content
 - (3) As radioactive as the radium content
 - (4) Twice as radioactive as the radium content.
- 9. Alpha rays are
 - (1) Positively charged
- (2) Negatively charged
- (3) Neutral
- (4) Both (1) and (3)
- 10. Which of the following does not characterize X-rays?
 - (1) Radiation can ionize gases.
 - (2) Radiation causes ZnS to fluoresce.
 - (3) Deflected by electric and magnetic field.
 - (4) Wavelengths are shorter than those of ultraviolet rays.
- 11. The rays are given off by a radioactive element from
 - (1) Nucleus
- (2) Valence electrons
- (3) All the orbits
- (4) Outer orbit

- 12. The alpha particles are
 - (1) High-energy electrons
 - (2) Positively charged hydrogen ions
 - (3) High-energy X-ray radiations
 - (4) Double positively charged helium nuclei
- 13. The emission of beta particles is from
 - (1) The valence shell of an atom
 - (2) The inner shell of an atom
 - (3) The nucleus due to the nuclear conversion: proton \rightarrow neutron + electron
 - (4) The nucleus due to the nuclear conversion: neutron \rightarrow proton + electron
- 14. A radioactive substance emanates:
 - (1) Alpha article
- (2) Beta particle
- (3) Gamma particle
- (4) All of these
- 15. A particle which is four times in mass and two times in charge that of proton is called
 - (1) Helium atom
- (2) An alpha particle
- (3) Deuteron
- (4) Tritium
- 16. Which of the following has the maximum penetrating power?
 - (1) α-particle
- (2) Proton
- (3) γ-particle
- (4) Positron
- 17. The phenomenon of radioactivity is associated with
 - (1) Decay of nucleus
 - (2) Fussion of nucleus
 - (3) Emission of electrons or protons
 - (4) Rearrangement in the extra nuclear electron
- 18. When passing through a magnetic field the largest deflection is experienced by
 - (1) α -rays
 - (2) β -rays
- (3) γ -rays
- (4) All equal

(1) At MB.

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1)3

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(3) 3

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- 19. Atoms with the same atomic number and different mass numbers are called
 - (1) Isobars

- (2) Isomers (3) Isotones (4) Isotopes
- 20. How many α-particles are emitted in the nuclear transformation: $_{84}Po^{215} \longrightarrow {}_{82}Pb^{211} + ?_{2}He^{4}$
 - (1)0
- (2) 1
- (3)2
- (4) 3
- 21. Which one of the following does not consist of charged particles of matter?
 - (1) α-particles
- (2) β-rays
- (3) γ-rays

(1) 2

- (4) Anode rays 22. Group displacement law was given by
- (1) Becquerel
- (2) Rutherford
- (3) Mendeleef
- (4) Soddy and Fazan
- 23. From the reaction given below, deduce the group of polonium in the periodic table (Pb belongs to group 14)
 - $_{84}Po^{210} \longrightarrow _{82}Pb^{206} + _{2}He^{4}$

(2) 14

- (3)6
- (4) 16

Which is different in isotopes of a	an element?
Which 18 difference of the Which 18 difference o	
Which is carry (1) Atomic number number	
(1) Atomotic (2) Mass number	
(2) Mass name (3) Number of protons	
(3) Number of P (4) Number of electrons (4) Number of electrons (5) the same mass num	ber but having different
(4) Number of electrons (4) Number of electrons (5) Atoms with the same mass num	S SALLOINI
nilClear	sobars
(1) Isotopes	sotones
(3) Isochores (4) Isochores	nt to
(3) Isocnores 26. One curie of activity is equivalent (1) 3.7×10^7 disintegrations per	second
27 Y III HISIMOBIATIONS POL	
(1) 3.7 × 10 ¹⁰ disintegrations per (2) 3.7 × 10^{10} disintegrations per	second
(3) 3.7 × 10 ⁴ disintegrations per	Second
(4) None	
(4) Note	oresents isobars?
v^{40} and Na^{23} (2)	He and the
$^{(3)}$ $_{12}$ Mg ²⁴ and 12 Mg ²⁵ (4)	$_{19}$ K ⁴⁰ and $_{20}$ Ca ⁴⁰
28. One atomic unit is equal to	1 400 × 10=2 area
$(1) 1.492 \times 10^{-3} \text{ ergs}$ (2)	1.492×10^{-2} ergs
(3) $1.492 \times 10^{-10} \text{ ergs}$ (4)	None of these
29. An element is isobaric with the electronic arrangement of the el	ement is $1s^2 2s^2 2p^6 3s^2 3p^6$
electronic arrangement of the el 4s ² . How many neutrons does ea	ch atom of the element carry
4s ² . How many neutrons does ear in its nucleus?	
(2) (3)	18 (4) 16
(1) 22 (2) 20 (3) 30. Two nuclei are not identical bu	t have the same number of
1 Thorn ore	
(a) I 1 (3)	Isotones (4) None
(1) Isotopes (2) Isotoars (3) 31. The density of nucleus is about	times the density
of atom	- 10
$\begin{array}{ccc} \text{(1) } 10^{-14} & \text{(2) } 10^{12} & \text{(3)} \end{array}$	
(1) 10^{-14} (2) 10^{12} (3) 32. The ratio of the radii of the ato	$\frac{\text{m to the fluores}}{10^2 \cdot 1}$ (4) $10^3 : 1$
32. The ratio of the radii of the and (1) $10^4 : 1$ (2) $10^{-4} : 1$ (3)	in stomic nucleus is of the
33 The distance between nucleon	S III atomic
) 25 Fermi
(1) 2 Fermi	10 Formi
(3) 100 Fermi (4) 34. The number of protons and neut	rons for most stable element is
34. The number of protons and neutrons) Even-even
(1) Even-odd	- 11 aven
(3) Odd-odd	agic numbers of both protons
(3) Odd-odd 35. In which of the following the manner present?	gag18
(1) 50 SH (-) 82 Had II	agic number
36. Which of the following has 2209 (1)	3) $_{92}U^{238}$ (4) $_{26}^{12}$
36. Which of the following has in $(1)_{13}Al^{27}$ (2) $_{83}Bi^{209}$ (3)	hose isotopes of closes, 8, 20,
(1) $_{13}Al^{27}$ (2) $_{83}Bi^{209}$ (37. Magic number elements are to the number of property of the number of the nu	hose isotopes of order hose isotopes or neutrons is 2, 8, 20, cotons or neutrons is 2, 8, 20,
37. Magic number elements	otons or neutrons

(1)In which the number of protons or neutrons is 2, 8, 20,

28, 50, 82, or 125

Nuclear Chemistry 6.49 (2) Which are relatively more abundant (3) Which are unusually stable (4) All of these 38. The SI unit of radioactivity is (2) Micro-curie (1) Curie (4) Becquerel (3) Rutherford 39. Which of the following elements an isodiaphere of $_{92}U^{235}$? $(2)_{82} Pb^{212}$ $(1)_{91}Pa^{231}$ $(4)_{92} Bi^{209}$ $(3)_{90}$ Th²³¹ **40.** During the transformation of ${}_{c}X^{a}$ to ${}_{d}Y^{b}$, the number of β-particles emitted are $(2) d + \frac{a-b}{2} + c$ (1) 2c - d + a - b $(3) d + \left(\frac{a-b}{2}\right) - c \qquad (4) \frac{a-b}{4}$ 41. Which of the following has a negative charge? (2) Positron (1) Neutron (4) Antiproton (3) Neutrino 42. A radioactive nucide emits γ -rays due to: (1) Presence of greater number of protons than neutrons (2) Nuclear transition from higher to lower energy state (3) Pressure of greater number of neutrons than protons (4) K-electron capture 43. In the radioactive decay: ${}_{Z}X^{A} \mathop{\rightarrow}\nolimits_{Z+1}Y^{A} \mathop{\rightarrow}\nolimits_{Z-1}Z^{A-4} \mathop{\rightarrow}\nolimits_{Z-1}Z^{*A-4}$ The sequence of emission is: (2) β , α , γ (1) β , γ , α (4) α , β , γ (3) γ , α , β 44. A certain radioactive material $_ZX^A$ starts emitting α and β particles successively such that the end product is $_{7-3}Y^{A-8}$. The number of α and β particles emitted are: (2) 2 and 1 respectively (1) 3 and 8 respectively (4) 4 and 3 respectively (3) 3 and 4 respectively 45. An element $_{90}$ Th²³⁴ looses an α -particle. If Th belongs to group III, the daughter element belongs to: (1) Zero group (2) Group II (3) Group III (4) Group I 46. If atomic mass of Th is 232.18 and its atomic no. is 90. If

it looses $6 - \alpha$ and $4 - \beta$ particles, the mass no. of finally

47. Which of the following processes result in an increase in

48. Atoms ${}_{7}X^A$, ${}_{8}Y^B$ and ${}_{9}Z^{17}$ are such that ${}_{8}Y$ is an isobar of $_{7}X$ and atom $_{9}Z^{17}$ is isotone of $_{8}Y$. Mass no. of X and no.

(2)208

(4)208.18

(2) Electron capture

(4) β-emission

stable element is:

(1) α-emission

(3) γ-emission

the atomic number of a nuclide?

of neutrons in Y are resectively:

(1)212

(3)226

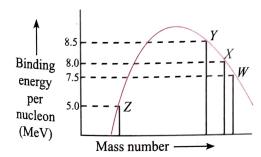
	(1) 8, 8	(2) 17, 7	59.	The end pro		•	
	(3) 9, 8	(4) 16, 8		$(1)_{83} Bi^{209}$	$(2)_{82} Pb^{207}$	$(3)_{83} Pb^{206}$	$(4)_{83}$ Bi ²⁰⁸ .
49.	Alpha decay of ₀₂ U ²³⁸ form	ns ₉₀ Th ²³⁴ . What kind of decay	60.	In which of	the following		,
	from ₉₀ Th ²³⁴ produces ₈₉ Ao			(1) α-emissi		(2) β-emissi	
	$(1) \alpha$	(2) β		(3) γ-emissio	on	(4) None	
	(3) β [⊕]	(4) γ-emission	61.	When oz U ²³⁸	decays it emit	s an α-particle	e. The new nuclide
50	Bi^{214} decays to A by α -e	mission. A then decays to B by		in turn emits	a β-particle to	give another ni	uclide X. The mass
50.	beta emission, which durth	her decays to C by another beta		number and	atomic numbe		
		ays to D by still another beta		(1) 234 and	91	(2) 234 and	96
	emission, and D decays b	y α-emission to form a stable		(3) 232 and	88	(4) 234 and	88
	isotope E. What is element		62.				ng two α - and one
	$(1)_{81}Tl^{207}$	$(2)_{80}$ Hg ²⁰⁶			the possible pr		
	$(3)_{79}$ Au ²⁰⁶	$(4)_{82} Pb^{206}$		$(1)_{89}Ac^{231}$	$(2)_{89}Ac^{23}$	5 (3) $_{89}$ Ac ²³⁶	$(4)_{89}$ Ac ²²⁷
51.	· ·	is the radius of nucleus of mass	63.	. Which of the	e following nu	clei is unstabl	e?
	v	Phose value is equal to 1.5×10^{-15}		$(1)_{5}B^{10}$	$(2)_{4} \text{Be}^{10}$	$(3)_{7}N^{14}$	$(4)_{8}O^{16}$
	metre. (Given 1 amu = 1.6	<u>-</u> ,	64.	$A_{89}Ac^{227}$ is a 1	nember of acti	nium series. A	nother member of
	What is the density of a m	cleus of mass number A?		the same ser	ries of		
	(1) $\frac{4}{3}\pi (1.5 \times 10^{-15})^3 A$	(2) $1.17 \times 10^{17} \text{ kg/cm}^3$		$(1)_{92}U^{235}$	$(2)_{90}$ Th ²³³	2 (3) $_{89}$ Ac ²²⁵	$(4)_{15}P^{34}$
	3			$(5)_{85}$ At ²¹⁷			
	(3) $1.17 \times 10^{-17} \text{ kg/m}^3$		65.	. The instabil	ity of a nucleu	s is due to	
52		adius of ${}_{6}C^{12}$ is 3×10^{-15} metre.		(1) High pro	ton electron ra	atio	
	What is density ratio of d	$c^{\prime}d_{\mathrm{H_2O}}$?		(2) High ele	ctron neutron	ratio	
	$(1) 1.76 \times 10^{17}$	$(2) 1.76 \times 10^{14}$		(3) Low pro	ton electron ra	tio	
	$(3) 17.6 \times 10^7$	$(4) 17.6 \times 10^{17}$		(4) Low pro	ton neutron rat	tio	
Rac	dioactive Disintegration Se	ries, n/p Ratio, Binding Energy	66	. Which of the	e following ele	ements belong	s to 4 <i>n</i> -series?
	dioactive Disintegration Se I Packing Fraction	ries, <i>n/p</i> Ratio, Binding Energy	66	Which of the (1) Pb-207	e following ele	ements belong (2) Bi-209	s to 4 <i>n</i> -series?
and		ries, <i>n/p</i> Ratio, Binding Energy	66.		e following ele		s to 4 <i>n</i> -series?
and	 1 Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decrease 			(1) Pb-207 (3) Pb-208	e following electric duct of $(4n + 2)$	(2) Bi-209 (4) Pb-206	
and	 d Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decrease (2) Remains constant 			(1) Pb-207 (3) Pb-208 . The end pro	duct of $(4n + 2)$	(2) Bi-209 (4) Pb-206 (2) disintegration	on series is
and	 1 Packing Fraction 3. In α-decay, n/p ratio: May increase or decrease Remains constant Decreases 		67	(1) Pb-207 (3) Pb-208 The end pro (1) ₈₂ Pb ²⁰⁴		(2) Bi-209 (4) Pb-206 (2) disintegratio (3) ₈₂ Pb ²⁰⁶	on series is
and 5	 1 Packing Fraction 3. In α-decay, n/p ratio: May increase or decrease Remains constant Decreases Increases 		67	(1) Pb-207 (3) Pb-208 The end pro (1) ₈₂ Pb ²⁰⁴ The end pro	duct of $(4n + 2n + $	(2) Bi-209 (4) Pb-206 (2) disintegration (3) ₈₂ Pb ²⁰⁶ es is	on series is (4) ₈₂ Pb ²⁰⁹
and 5	 1 Packing Fraction 3. In α-decay, n/p ratio: May increase or decrease Remains constant Decreases 		67 68	(1) Pb-207 (3) Pb-208 The end pro (1) ₈₂ Pb ²⁰⁴ The end pro (1) ₈₂ Pb ²⁰⁸	duct of $(4n + 2)$ $(2)_{82}Pb^{208}$ duct of 4n seri $(2)_{82}Pb^{207}$	(2) Bi-209 (4) Pb-206 (2) disintegratio (3) ₈₂ Pb ²⁰⁶ es is (3) ₈₂ Pb ²⁰⁹	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₃ Pb ²⁰⁴
and 5	 d Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decrease (2) Remains constant (3) Decreases (4) Increases 54. In β-decay n/p ratio (1) Remain unchanged (3) Increases 	(2) Decreases (4) May increase or decrease	67 68	(1) Pb-207 (3) Pb-208 • The end pro (1) ₈₂ Pb ²⁰⁴ • The end pro (1) ₈₂ Pb ²⁰⁸ • Radioactive in being	duct of $(4n + 2)$ $(2)_{82}Pb^{208}$ duct of 4n seri $(2)_{82}Pb^{207}$ disintegration	(2) Bi-209 (4) Pb-206 (2) disintegratio (3) ₈₂ Pb ²⁰⁶ es is (3) ₈₂ Pb ²⁰⁹	on series is (4) ₈₂ Pb ²⁰⁹
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and 5	 d Packing Fraction 3. In α-decay, n/p ratio: May increase or decrease Remains constant Decreases Increases In β-decay n/p ratio Remain unchanged Increases If n/p ratio is high, the number of a β-decay n/p ratio of a β-decay n/p ratio is high, the number of a β-decay n/p ratio of a β-dec	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle	67 68 69	(1) Pb-207 (3) Pb-208 The end pro (1) 82Pb ²⁰⁴ The end pro (1) 82Pb ²⁰⁸ Radioactive in being (1) An exoth (2) A sponta (3) A nuclea (4) A unimo	duct of $(4n + 2n)^{2}$ duct of $(4n + 2n)^{2}$ duct of $(4n)^{2}$ duct of $(4n)^{2}$ disintegration thermic change aneous process ar process elecular first-or	(2) Bi-209 (4) Pb-206 (2) disintegration (3) ₈₂ Pb ²⁰⁶ es is (3) ₈₂ Pb ²⁰⁹ differs from a	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ a chemical change
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and 5	 A Packing Fraction 3. In α-decay, n/p ratio: May increase or decrease Remains constant Decreases Increases In β-decay n/p ratio Remain unchanged Increases 55. If n/p ratio is high, the n The emission of a β- Neutron capture Losing a positron Any one of the above Who presented the theory Rutherford and Sodo 	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle e ry of radioactive disintegration? dy (2) Soddy and Fajan	67 68 69	(1) Pb-207 (3) Pb-208 • The end pro (1) 82 Pb ²⁰⁴ • The end pro (1) 82 Pb ²⁰⁸ • Radioactive in being (1) An exoth (2) A sponta (3) A nuclea (4) A unimo • The energy in	duct of $(4n + 2)$ $(2)_{82}$ Pb ²⁰⁸ duct of 4n seri $(2)_{82}$ Pb ²⁰⁷ disintegration hermic change aneous process ar process elecular first-or released during ergs	(2) Bi-209 (4) Pb-206 (2) disintegration (3) $_{82}$ Pb ²⁰⁶ es is (3) $_{82}$ Pb ²⁰⁹ differs from a der reaction (4) the fission of (2) 9.0 × 10 ¹	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ (chemical change) 1 kg of uranium is 0 ergs
and 5	 d Packing Fraction 3. In α-decay, n/p ratio: May increase or decrease Remains constant Decreases Increases In β-decay n/p ratio Remain unchanged Increases 55. If n/p ratio is high, the n The emission of a β- Neutron capture Losing a positron Any one of the above Rutherford and Sode Thomson and Ruthe 	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle e ry of radioactive disintegration? dy (2) Soddy and Fajan rford	67 68 69	(1) Pb-207 (3) Pb-208 • The end pro (1) $_{82}$ Pb ²⁰⁴ • The end pro (1) $_{82}$ Pb ²⁰⁸ • Radioactive in being (1) An exoth (2) A sponta (3) A nuclea (4) A unimo • The energy (1) 9×10^{23} (3) 9.0×10^{21}	duct of $(4n + 2)$ $(2)_{82}$ Pb ²⁰⁸ duct of 4n seri $(2)_{82}$ Pb ²⁰⁷ disintegration hermic change aneous process ar process elecular first-or released during ergs 18 ergs	(2) Bi-209 (4) Pb-206 (2) disintegration (3) $_{82}$ Pb ²⁰⁶ es is (3) $_{82}$ Pb ²⁰⁹ differs from a der reaction (4) 9.0 × 10 ¹ (4) 9.0 × 10 ⁸	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ (4) chemical change 1 kg of uranium is 0 ergs
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and 5	 A Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decrea (2) Remains constant (3) Decreases (4) Increases (4) In β-decay n/p ratio (1) Remain unchanged (3) Increases (5) If n/p ratio is high, the n (1) The emission of a β- (2) Neutron capture (3) Losing a positron (4) Any one of the above (5) Who presented the theor (1) Rutherford and Sodo (3) Thomson and Ruthe (4) Hahn and Strassman 57. Starting from radium, the 	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle e ry of radioactive disintegration? dy (2) Soddy and Fajan rford in e radioactive disintegration process	67 68 69	(1) Pb-207 (3) Pb-208 The end pro (1) $_{82}$ Pb ²⁰⁴ The end pro (1) $_{82}$ Pb ²⁰⁸ Radioactive in being (1) An exoth (2) A sponta (3) A nuclear (4) A unimo The energy in the energy in t	duct of $(4n + 2)$ $(2)_{82}$ Pb ²⁰⁸ duct of 4n seri $(2)_{82}$ Pb ²⁰⁷ disintegration hermic change aneous process ar process alecular first-or released during ergs 18 ergs re value of page	(2) Bi-209 (4) Pb-206 (2) disintegration (3) $_{82}$ Pb ²⁰⁶ es is (3) $_{82}$ Pb ²⁰⁹ differs from a significant of the fission of (2) 9.0 × 10 ¹⁰ (4) 9.0 × 10 ⁸⁰ eking fraction	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ (4) ₈₂ Pb ²⁰⁴ (4) chemical change 1 kg of uranium is 0 ergs 1 ergs 1 ergs 1 indicates that the
and 5	A Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decre (2) Remains constant (3) Decreases (4) Increases 54. In β-decay n/p ratio (1) Remain unchanged (3) Increases 55. If n/p ratio is high, the n (1) The emission of a β- (2) Neutron capture (3) Losing a positron (4) Any one of the above (1) Rutherford and Sode (3) Thomson and Ruthe (4) Hahn and Strassman 57. Starting from radium, the terminates when the fol	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle e ry of radioactive disintegration? dy (2) Soddy and Fajan rford in e radioactive disintegration process lowing is obtained	67 68 69	(1) Pb-207 (3) Pb-208 • The end pro (1) $_{82}$ Pb ²⁰⁴ • The end pro (1) $_{82}$ Pb ²⁰⁸ • Radioactive in being (1) An exoth (2) A sponta (3) A nuclear (4) A unimo • The energy in the ene	duct of $(4n + 2)$ $(2)_{82}$ Pb ²⁰⁸ duct of 4n seri $(2)_{82}$ Pb ²⁰⁷ disintegration hermic change neous process ar process elecular first-or released during ergs 18 ergs re value of page	(2) Bi-209 (4) Pb-206 (2) disintegration (3) $_{82}$ Pb ²⁰⁶ es is (3) $_{82}$ Pb ²⁰⁹ differs from a der reaction (4) 9.0 × 10 ⁸ exing fraction (2) Very stab	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ (4) ₈₂ Pb ²⁰⁴ (4) chemical change 1 kg of uranium is 0 ergs 1 ergs 1 ergs 1 indicates that the
and 5	 A Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decrease (2) Remains constant (3) Decreases (4) Increases (4) In β-decay n/p ratio (1) Remain unchanged (3) Increases (5) If n/p ratio is high, the n (1) The emission of a β- (2) Neutron capture (3) Losing a positron (4) Any one of the above (5) Who presented the theor (1) Rutherford and Sode (3) Thomson and Ruthe (4) Hahn and Strassman 57. Starting from radium, the terminates when the fol (1) Radon (2) Lead 	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle e ry of radioactive disintegration? dy (2) Soddy and Fajan rford in e radioactive disintegration process lowing is obtained (3) Uranium (4) Thorium	67 68 69 70	(1) Pb-207 (3) Pb-208 . The end pro (1) ₈₂ Pb ²⁰⁴ . The end pro (1) ₈₂ Pb ²⁰⁸ . Radioactive in being (1) An exoth (2) A sponta (3) A nuclea (4) A unimo . The energy (1) 9 × 10 ²³ (3) 9.0 × 10 . The negative isotope is (1) Unstable (3) Artificia . The binding	duct of $(4n + 2)$ (2) $_{82}$ Pb ²⁰⁸ duct of 4n seri (2) $_{82}$ Pb ²⁰⁷ disintegration hermic change aneous process ar process ar process ar process ar eleased during ergs 18 ergs we value of pace 18 ergs	(2) Bi-209 (4) Pb-206 (2) disintegration (3) $_{82}$ Pb ²⁰⁶ es is (3) $_{82}$ Pb ²⁰⁹ differs from a der reaction (the fission of (2) 9.0 × 10 ⁸ (4) 9.0 × 10 ⁸ eking fraction (2) Very stable (4) Stable	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ (4) chemical change 1 kg of uranium is o ergs ergs indicates that the
and 5	 A Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decrease (2) Remains constant (3) Decreases (4) Increases (4) In β-decay n/p ratio (1) Remain unchanged (3) Increases (5) If n/p ratio is high, the n (1) The emission of a β- (2) Neutron capture (3) Losing a positron (4) Any one of the above (5) Who presented the theor (1) Rutherford and Sode (3) Thomson and Ruthe (4) Hahn and Strassman 57. Starting from radium, the terminates when the fol (1) Radon (2) Lead 	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle e ry of radioactive disintegration? dy (2) Soddy and Fajan rford in e radioactive disintegration process lowing is obtained (3) Uranium (4) Thorium les and 6 β-particles. The n/p ratio	67 68 69 70	(1) Pb-207 (3) Pb-208 . The end pro (1) ₈₂ Pb ²⁰⁴ . The end pro (1) ₈₂ Pb ²⁰⁸ . Radioactive in being (1) An exoth (2) A sponta (3) A nuclea (4) A unimo . The energy (1) 9 × 10 ²³ (3) 9.0 × 10 . The negative isotope is (1) Unstable (3) Artificia . The binding	duct of $(4n + 2)$ (2) $_{82}$ Pb ²⁰⁸ duct of 4n seri (2) $_{82}$ Pb ²⁰⁷ disintegration hermic change aneous process ar process ar process ar process ar eleased during ergs 18 ergs we value of pace 18 ergs	(2) Bi-209 (4) Pb-206 (2) disintegration (3) $_{82}$ Pb ²⁰⁶ es is (3) $_{82}$ Pb ²⁰⁹ differs from a der reaction (the fission of (2) 9.0 × 10 ⁸ (4) 9.0 × 10 ⁸ eking fraction (2) Very stable (4) Stable	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ (4) ₈₂ Pb ²⁰⁴ (4) chemical change 1 kg of uranium is 0 ergs 1 ergs 1 ergs 1 indicates that the
and 5	1 Packing Fraction 3. In α-decay, n/p ratio: (1) May increase or decre (2) Remains constant (3) Decreases (4) Increases 54. In β-decay n/p ratio (1) Remain unchanged (3) Increases 55. If n/p ratio is high, the n (1) The emission of a β- (2) Neutron capture (3) Losing a positron (4) Any one of the above (1) Rutherford and Sode (3) Thomson and Ruthe (4) Hahn and Strassman 57. Starting from radium, the terminates when the fol (1) Radon (2) Lead 58. 92U ²³⁸ emits 8 α-particl	(2) Decreases (4) May increase or decrease ucleus tends to stabilize by: particle e ry of radioactive disintegration? dy (2) Soddy and Fajan rford an e radioactive disintegration process lowing is obtained (3) Uranium (4) Thorium les and 6 β-particles. The n/p ratio is	67 68 69 70	(1) Pb-207 (3) Pb-208 . The end pro (1) ₈₂ Pb ²⁰⁴ . The end pro (1) ₈₂ Pb ²⁰⁸ . Radioactive in being (1) An exoth (2) A sponta (3) A nuclea (4) A unimo . The energy (1) 9 × 10 ²³ (3) 9.0 × 10 . The negative isotope is (1) Unstable (3) Artificia . The binding	duct of $(4n + 2)$ $(2)_{82}$ Pb ²⁰⁸ duct of 4n seri $(2)_{82}$ Pb ²⁰⁷ disintegration hermic change aneous process released during ergs 18 ergs re value of page	(2) Bi-209 (4) Pb-206 (2) disintegration (3) $_{82}$ Pb ²⁰⁶ es is (3) $_{82}$ Pb ²⁰⁹ differs from a der reaction (the fission of (2) 9.0 × 10 ⁸ (4) 9.0 × 10 ⁸ eking fraction (2) Very stable (4) Stable	on series is (4) ₈₂ Pb ²⁰⁹ (4) ₈₂ Pb ²⁰⁴ (4) chemical change 1 kg of uranium is o ergs ergs indicates that the

(4) 6

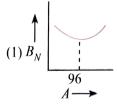
6.50 Physical Chemistry

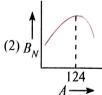
- 73. Total binding energy of α-particles is
- (1) 28.3 MeV
- (2) 2.83 MeV
- (3) 20.5 MeV
- (4) 0.283 MeV
- 74. The energy equivalent to 1 amu is
 - (1) 931.5 MeV
- (2) 93.15 MeV
- (3) 460 MeV
- (4) 554 MeV
- 75. Atomic weight of Th is 232 and its atomic number is 90. The number of α - and β -particles which will be lost so that an isotope of lead (atomic weight 208 and atomic number 82) is produced is
 - $(1) 4\alpha + 6\beta$
- $(2) 6\alpha + 4\beta$
- $(3) 8\alpha + 2\beta$
- (4) $10\alpha + 2\beta$
- 76. Least branching is found in which of the following radioactive series?
 - (1) 4n + 2
- (2) 4n
- (3) 4n + 3
- (4) 4n + 1
- 77. The atomic mass and atomic number of lead are 208 and 82. The atomic mass and atomic number of bismuth are 209 and 83. The neutron/proton ratio in an atom
 - (1) Is higher in lead than in bismuth
 - (2) Is lower in lead than in bismuth
 - (3) Is equal in both lead and bismuth
 - (4) None of these
- 78. When n/p ratio of an isotope is greater than the stable isotope of that element, it emits
 - (1) β-particles
- (2) α-particles
- (3) Neutron
- (4) Positron
- 79. Which of the following is artificial radioactive series?
 - (1) 4n + 1
- (2) 4n + 2

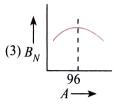
- (3) 4n
- (4) 4n + 3
- 80. All nuclides exhibit radioactivity when the atomic number exceeds
 - (1) 80
- (2)83
- (3)90
- (4)92
- 81. Binding energy per nucleon versus mass number for W, X, Y, Z are indicated on the curve.

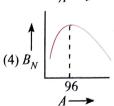


- The process that would release energy is:
- $(1) X \rightarrow Y + Z$
- (2) $W \rightarrow X + Z$
- (3) $W \rightarrow 2Y$
- $(4) Y \rightarrow 2Z$
- 82. The dependence of binding energy per nucleon, B_N , on the mass number A is represented by:



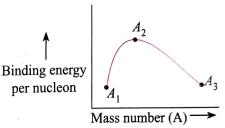








83. In the following graph, binding energy per nucleon is plotted against mass number (A). There element A_1 , A_2 and A_3 are located in the graph. Select the false statement about the graph.



- (1) A₂ is metallic element
- (2) Element A₃ is less stable than A₂
- (3) Element A_1 is more stable than both A_2 and A_3
- (4) Element A₂ is more stable than A₁
- 84. The mass defect for the formation of C¹² is 0.10242 amu. Its binding energy would be
 - (1) 95.35 MeV
- (2) 95.35 eV
- (3) 9.535 eV
- (4) 9.535 MeV
- 85. The binding energy per nucleon of O¹⁶ is 7.97 MeV and that of O¹⁷ is 7.75 MeV. The energy in MeV required to remove a neutron from O¹⁷ is
 - (1)7.86
- (2) 3.64
- (3)4.23
- (4) 3.52
- 86. How much heat would be developed per hour from 1 curie of C¹⁴ source if all the energy of beta decay were imprisoned? Atomic masses of C14 and N14 are 14.00324 and 14.00307 amu respectively.
 - (1) 3.36 J
- (2) 3.37 J
- (3) 3.38 J
- (4) 3.39 J
- 87. In the reaction ${}_{1}H^{2} + {}_{1}H^{3} \rightarrow {}_{2}He^{4} + {}_{0}n^{1}$ if binding energies of $_{1}H^{2}$, $_{1}H^{3}$ and $_{2}He^{4}$ are respectively a, b, and c (in MeV), then the energy released in this reaction is:
 - (1) a + b + c
- (2) a + b c
- (3) c (a + b)
- (4) c + a b
- 88. Consider the following decay ${}_{Z}X^{A} \rightarrow {}_{Z+1}Y^{A} + {}_{-1}e^{0}$, X is unstable because:
 - (1) Its nucleus has excess energy
 - (2) $\frac{n}{p}$ ratio is high



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- (3) $\frac{n}{n}$ ratio is low
- (4) None of these
- **89.** Consider the following decay $_{Z}X^{A} \rightarrow _{Z^{-1}}Y^{A} + _{+1}e^{0}$, X is unstable because:
 - (1) Its nucleus has excess energy
 - (2) $\frac{n}{p}$ ratio is high
 - (3) $\frac{n}{n}$ ratio is low
 - (4) None of these
- 90. ₆₇Ho¹⁶⁵ is stable isotope. ₆₇Ho¹⁵⁰ is expected to disintegrate
 - (1) α-emission
- (2) β -emission
- (3) Positron emission
- (4) y-emission
- 91. ₁H¹ is a stable isotope. ₁H³ is expected to disintegrated by:
 - (1) α -emission
- (2) β -emission
- (3) Positron emission
- (4) Proton emission
- 92. Emission of β -particle is equivalent to:
 - (1) Increase of one proton only
 - (2) Decrease of one neutron only
 - (3) Both (1) and (2)
 - (4) None of these
- 93. $_{92}U^{235} + _{0}n^{1} \longrightarrow _{56}Ba^{139} + _{36}Kr^{94} + 3_{0}n^{1} + 200 \text{ MeV}$ Total energy released (in MeV) after 5th stage of fission is:
 - (1)48600
- (2) 16200
- (3)24200
- (4) None of these

Rate of Disintegration, Half and Average Life

- 94. Radioactive decay is a reaction of
 - (1) Zero order
- (2) First order
- (3) Second order
- (4) Third order
- 95. Quantity of radioactive material which undergoes 10⁶ disintegrations per second is called
 - (1) Becquerel
- (2) Rutherford
- (3) Curie
- (4) Faraday
- 96. One curie of activity is equivalent to
 - (1) 3.7×10^{17} disintegrations per second
 - (2) 3.7×10^{10} disintegrations per second
 - (3) 3.7×10^{14} disintegrations per second
 - (4) 3.7×10^3 disintegration per second
- 97. The unit for radioactive constant is
 - (1) time
- (2) time mol^{-1}
- (3) time⁻¹
- (4) mol time⁻¹
- **98.** The relation between half-life period $(t_{1/2})$ and disintegration constant (λ) is expressed as

$$(1) \lambda = \frac{0.693}{t_{1/2}}$$

(2)
$$\lambda = 0.693 \ t_{1/2}$$

(3)
$$\lambda = \frac{693}{t_{1/2}}$$

(4) $\lambda = 693 t_{1/2}$

- 99. If 2 g of an isotope has a half-life of 7 days, the half life of 1 g sample is
 - (1) 3.5 days (2) 7 days
- (3) 14 days (4) 28 days
- 100. Half-life of a radioactive disintegration $(A \rightarrow B)$ having rate constant 231 s⁻¹ is
 - (1) 3.0×10^{-2} s
- (2) 3×10^{-3} s
- (3) 3.3×10^{-2} s
- (4) 3.3×10^{-3} s
- 101. C¹⁴ has a half-life of 5760 years. 100 mg of the sample containing 14C is reduced to 25 mg in
 - (1) 11520 years
- (2) 2880 years
- (3) 1440 years
- (4) 17128 years
- 102. If 3/4 quantity of a radioactive substance disintegrates in 2 hours, its half-life period will be
 - (1) 15 min
- $(2) 30 \min$
- (3) 60 min
- (4) 90 min
- 103. The initial mass of a radioactive element is 40 g. How many grams of it would be left after 24 years if its half-life period is of 8 years?
 - (1) 2
- (2)5
- (3) 10
- (4)20
- 104. A radioisotope has a half life of 10 days. If today there is 125 g of it left, what was its mass 40 days earlier?
 - (1) 600 g
- (2) 1000 g
- (3) 1250 g
- 105. The half-life periods of four isotopes are given below:
 - **i.** 7.6 years
- ii. 4000 years
- iii. 6000 years
- iv. 3.2×10^5 years

Which of the above isotopes is most stable?

- (1) iv
- (2) iii
- (3) ii
- (4) i
- 106. Ra²²⁶ has half life of 1600 years. The number of disintegration per second per gram is
 - (1) 3.7×10^{10}
- $(2) 9.2 \times 10^6$
- $(3) 3.7 \times 10^9$
- $(4) 3.7 \times 10^8$
- 107. The decay constant of Ra²²⁶ is 1.37×10^{-11} s⁻¹. A sample of Ra²²⁶ having an activity of 1.5 millicurie will contain
 - (1) 4.05×10^{18} atoms
- (2) 3.7×10^{17} atoms
- (3) 2.05×10^{15} atoms
- $(4) 4.7 \times 10^{10}$ atoms
- 108. The number of α -particles emitted per second by 1 g of Ra^{226} is 3.7×10^{10} . The decay constant is
 - (1) 1.39×10^{-11} s⁻¹
- (2) 13.9×10^{-11} s⁻¹
- (3) $139 \times 10^{-11} \, \mathrm{s}^{-1}$
- $(4)\ 0.139 \times 10^{-11}\ s^{-1}$
- 109. Radioactivity of a radioactive element remains 1/10 of the original radioactivity after 2.303 seconds. The half life period is
 - (1) 2.303
- (2) 0.2303

(3)693

- (4) 0.693
- 110. At radioactive equilibrium, the ratio of two atoms A and B are 3.1×10^9 : 1. If half life of A is 2×10^{10} years, then what is the half life of B?
 - (1) 6.45 yrs
- (2) 4.65 yrs
- (3) 5.46 yrs
- (4) 5.64 yrs

fraction of the substance will remain after 6400 min?

(1) 1/16(2) 1/4(3) 1/8(4) 1/2121. If 8.0 g of radioactive isotope has a half life of 10 hours, the half life of 2.0 g of the same substance is (1) 2.5 hours (2) 5.0 hours (3) 10 hours (4) 40 hours 122. If two light nuclei are fused together in nuclear reaction, the average energy per nucleon (1) Increases (2) Decreases (3) Cannot be determined (4) Remains same 123. A certain nuclide has a half life period of 30 min. If a sample containing 600 atoms is allowed to decay for 90 min, how many atoms will remain? (1) 200 atoms (2) 450 atoms (3) 75 atoms (4) 150 atoms 124. A substance is kept for 2 hours and three-fourth of that substance disintegrates during this period. The half life of the substance is (1) 2 hr(2) 1 hr (4) 4 hr $(3) 30 \min$ 125. The decay of a radioactive element follows first order kinetics. Thus, (1) Half-life period = a constant/K, where K is decay constant (2) The rate of decay is independent of temperature (3) The rate can be altered by changing chemical conditions (4) The element will be completely transformed into new element after expiry of two half-life period 126. After three half lives, the percentage of fraction of amount left is (1) 6.35(2) 12.5(3)50(4)75127. A radioactive sample had an initial activity of 56 dpm. After 69.3 minutes, it was found to have an activity of 28 dpm. Find the number of atoms in a sample having an activity of 100 dpm. (1)693(2) 100(3) 1000(4) 10,000 128. A radioactive sample has initial activity of 28 dpm, 30 minutes later its activity is 14 dpm. How many atoms of nuclide were present initially? (1)2800(2) 1212(4)2802(3)528129. A sample of radioactive substance is found 90% of its initial amount after one day. What % of the original sample can be

(2)72.9

time interval between the stages to 50% and 87.5% decay

will be:

(4) 65.61

6.54	Physical Chemistry				
	(1) 100 min	(2) 50 min	138. Upon irradiating	g californium with neutrons a new nuc	
	(3) 200 min	(4) 25 min			
131.	α-emission, while starting with 1 mol	sec) decay to Pb ⁸² ($t_{1/2} = 161 \text{ sec}$) by Pb ²¹⁴ is a β -emitter. In an experiment e of pure Po ²¹⁸ , how much time would	radioactivity due	er 90 min. of irradiation, the observe to nuclide was 100 dis/min. How make the leide were present initially? (2) 3.46×10^4	
	maximum?	number of nuclei of ₈₂ Pb ²¹⁴ to reach	(3) 1900	(4) 800	
	(1) 147.5 (3) 182	(2) 247.5 (4) 304		an) life of a radio nuclide which decays	i by
132.	is β -emitter. Their of 1:2. What should be at time $t = 0$, so that	nuclei A and B . A is a α -emitter and B disntegration constant are in the ratio of the the number of atoms ratio of A and B initially probability of getting of α and		$\lambda_1 = 1.8 \times 10^{-2} \text{ sec}^{-1}$ $\lambda_2 = 1.8 \times 10^{-3} \text{ sec}^{-1}$ (2) 500 ass	
	β-particles are same			(2) 500 sec	
	(1) 2 : 1	(2) 4 : 1	(3) 50 sec	(4) None of these	
	disintegrate at the rat At 3.55 P.M. of the s	(4) 1:4 nical preparation was observed to e of 2140 counts/minutes at 12.35 P.M. same day, the disintegration rate of the 5 count/minutes. What is the half-life	1.0 mL sample of the animal blood s equilibrium to be e activity to 10 dpm	nine the volume of blood in an animal solution of 10 ³ dpm of ₁ H ³ is injected in tream. After sufficient time for circulate established, 2 mL of blood is found to hat. The volume of blood in animal is:	ito
	(1) 50 min	(2) 100	(1) 199 mL	(2) 198 mL	
	(3) 200 min	(2) 100 min(4) None of these	(3) 200 mL	(4) 20 mL	
134.	A radioactive nuclide second, Its decay cor	e is produced at a constant rate of α per astant is λ . If N_0 be the no. of nuclei at mum number of nuclei possible are : (2) α/λ	mixture at time t = the ratio of activition	ities of two radio nuclides X and Y in 0 was found to be $4:1$. After two hourses become $1:1$. If the $t_{1/2}$ of radio nuclide Y is: (2) 20	rs.
	(2)210		(3) 30	(4) 40	
	$(3) N_0 + \frac{\alpha}{\lambda}$	$(4) \frac{\lambda}{\sigma} + N_0$	142. The radioactive de	ecay $_{83}Bi^{211} \longrightarrow _{81}Tl^{207}$, takes place i	II
1	mixed in equal amou	and B of atomic mass X and Y are nt by mass, After 20 days, their mass: 4 Isotope A has a half-life of 1 day,	$_{83}$ Bi ²¹¹ $(t_{1/2} = 130)$ vessel after 520 sec	sel at 27°C. Starting with 2 moles of sec), the pressure development in the will be:	e e
t	the half-life of isotop	e <i>B</i> is:	(1) 1.875 atm	(2) 0.2155 atm	
	Y .	X	(3) 0.4618 atm	(4) 4.168 atm	
((1) 1.11 $\frac{Y}{X}$ day	(2) $0.11 \frac{X}{Y}$ day	143. A fresh radioactive	mixture contains short lived species	1
	(3) 0.6237 day	(4) 1.10 day	per minute. 20 min	g α -particles initially of 8000 α -particle autes later they emit at the rate of 3500	0
1 <i>E</i>	0 min respectively. A to be eight times tha	des A and B have half-lives 50 min and a fresh sample contains the nuclide of t of A . How much time should elapse nuclides of A becomes double of B ?	B are 10 minutes an of activities of $A : B$	ute. If the half-lives of the species A and 500 hours respectively, then the ratio 3 in the intial mixture was:	i ,
	1) 30	(2) 40	(1) 4 : 6	(2) 6 : 4	15
	3) 50	(4) 100	(3) 3 : 4	(4) 3 : 1	
137. A		of 22 years. The decays follows two	Artificial Transmutation of Radioactivity	, Nuclear Reactions and Applications	
1	Ac ²²⁷ (λ)		144. In a chain reaction un different materials.	ranium atom gets fissioned forming two The total weight of these put together	133

(1) More than the weight of parent uranium atom(2) Less than the weight of parent uranium atom

(4) Neither more nor less

(3) More or less depends upon experimental conditions

 $\frac{\lambda_2}{}$ Fr²²³ (% yield = 98)

(2) 0.00063, 0.03087

(4) None of these

What are the decay constants (λ) for Th and Fr respectively?

(1) 0.03087, 0.00063

(3) 0.02, 0.98

Which one of the following nuclear transformations is (n, p) type? $(1)_{3}^{(n,p')} \stackrel{?}{\downarrow}_{1}^{1} H^{1} \longrightarrow {}_{4}\text{Be}^{7} + {}_{0}n^{1}$

 $(2)_{33}^{As^{75}} + {}_{2}^{He^4} \longrightarrow {}_{35}^{Br^{78}} + {}_{0}^{n^1}$

 $(3)_{83}^{(6)} Bi^{209} + {}_{1}H^{2} \longrightarrow {}_{84}Po^{210} + {}_{0}n^{1}$ $(4)_{21}^{85}Sc^{45} + {}_{0}n^{1} \longrightarrow {}_{20}Ca^{45} + {}_{1}H^{1}$

146. An example of nuclear fusion reaction is

 $(1)_{90} \text{Th}^{233} + {}_{0} n^{1} \longrightarrow {}_{90} \text{Th}^{234}$

 $(2)_{13}Al^{27} + _{2}He^{4} \longrightarrow _{15}P^{30} + _{0}n^{1}$

 $(3)_{2}He^{3} + {}_{2}He^{3} \longrightarrow {}_{2}He^{4} + 2_{1}H^{1}$

 $(4)_{92}U^{239} \longrightarrow {}_{93}Np^{239} + {}_{0}e^{1}$

147. The reaction $_{92}U^{235} + _{0}n^{1} \longrightarrow _{56}Ba^{140} + _{36}Kr^{93} + _{3}n^{1}$ represents

(1) Artificial radioactivity (2) Nuclear fission

(3) Nuclear fusion

(4) None of these

148. C14 in upper atmosphere is generated by the nuclear

 $(1)_{7}N^{14} + {}_{1}H^{1} \longrightarrow {}_{6}C^{14} + {}_{+1}e^{0} + {}_{1}H^{1}$

 $(2)_{7}N^{14} \longrightarrow {}_{6}C^{14} + {}_{1}_{1}e^{0}$

 $(3)_{7}N^{14} + {}_{0}n^{1} \longrightarrow {}_{c}C^{14} + {}_{1}H^{1}$

 $(4)_{7}N^{14} + {}_{1}H^{1} \longrightarrow {}_{6}C^{11} + {}_{2}He^{4}$

149. In a nuclear reactor, chain reaction is controlled by introducing

(1) Iron rod

(2) Cadmium rod

(3) Graphite rod

(4) Gold rod

150. In a nuclear explosion, the energy is released in the form of

(1) Thermal energy

(2) Kinetic energy

(3) Potential energy

(4) Electrical energy

151. Which one of the following is a major hurdle in finding ways to properly harness nuclear fusion energy on a commercial scale in an effort to solve nuclear crisis?

(1) Purifications of raw materials

(2) Finding safe ways to disposing off the waste products

(3) To maintain high temperature for the reaction

(4) Non-availability of skilled scientists

152. Breeder reactors are nuclear reactors that are capable of converting non-radioactive isotopes into radioactive fissionable isotopes, which can be used for generating energy. U-238, a non-radioactive isotope is thus converted into radioactive

(1) U-234

(2) Pu-94

(4) C-13

153. In which of the following radioactive isotopes I-131 is not (3) I-131

(1) In the diagnosis of lever and kidney disorder

(2) Treatment of thyroid diseases

(3) Increasing absorption of calcium in the body

(4) For locating tumors in brain.

154. An atom of radium combines with two atoms of chlorine to form RaCl, molecule. The radioactivity of RaCl, will be

(1) Zero

(2) 1/3 of the same quantity of radium

(3) As much as that of same quantity of radium

(4) 1/4 of the same quantity of radium

155. Mass number of a nuclide is 216, its approximate radius in fermi units is

(1)6.0

(2)7.0

(3) 8.0

(4) 8.4

156. The I-128 has no therapeutic value because

(1) It is poisonous

(2) It is very stable

(3) It decays quickly and loses radioactivity

(4) It is not radioactive

157. The radioactivity due to C-14 isotope (half life = 6000 years) of a sample of wood from an ancient tomb was found to be nearly half that of fresh wood. The tomb is there for about

(1) 3000 year old

(2) 6000 year old

(3) 9000 year old

(4) 12000 year old

158. Which of the following ages cannot be determined by radioactive carbon dating?

(1) Remains of the animal

(2) Samples of rock from old mountain

(3) A 1000-year-old tree

(4) An old piece of wood

159. The age of most ancient geological formations is estimated by

(1) C-14 dating method

(2) K-Ag method

(3) U-Pb method

(4) Ra-Rn method

160. The source of enormous energy of sun is

(1) Fusion of hydrogen to form helium

(2) Fission of uranium

(3) Fusion of deuterium and tritium

(4) Fusion to tritium to form helium

161. Which of the following projectiles is the best for bombarding

(1) α-particle

(2) Proton

(3) Deuteron

162. Which of the following nuclear changes is incorrect? ${}^{(1)}_{20}\text{Ca}^{40} + {}_{0}n^{1} \longrightarrow {}_{19}\text{K}^{40} + {}_{1}\text{H}^{1}$

(2) $_{12}^{20}Mg^{24} + \alpha \longrightarrow {}_{14}^{13}Si^{27} + {}_{0}^{11}$

(3) ${}_{48}\text{Cd}^{113} + {}_{0}n^{1} \longrightarrow {}_{48}\text{Cd}^{112} + {}_{-1}e^{0}$

 $(4)_{20}Co^{43} + \alpha \longrightarrow_{21}Si^{46} + _{1}H^{1}$

163. Which of the following particles is emitted in the nuclear reaction: ${}_{13}Al^{27} + {}_{2}He^{4} \longrightarrow {}_{14}P^{30} + ...?$

 $(4)_{1}H^{2}$

6.56 Physical Chemistry	
164. When $_{17}C1^{35}$ undergoes (n, p) reaction, the radioisotope	
formed is	(2) Uranium and stable lead
$(1)_{15}P^{32} \qquad (2)_{16}S^{35} (3)_{16}S^{34} (4)_{15}P^{34}$	(3) Carbon and stable carbon
165. Neutrons are more effective projectiles than protons because there	(1) 2222
they	175. The radioisotope used in the treatment of cancer is
(1) Are attracted by the nuclei	(1) $C-12$ (2) $Co-60$ (3) $I-31$ (4) $P-31$
(2) Are not repelled by the nuclei	176. ₆ C ¹⁴ in the upper atmosphere is formed by the action of
(3) Travel with high speed	neutron on
(4) None of these	$(1)_{7}N^{14}$ $(2)_{8}O^{17}$ $(3)_{6}C^{12}$ $(4)_{8}O^{18}$
166. A method which uses radioactivity for determining the age of prehistoric materials is called	2, 11 12, and gotte of the principle of
(1) Carbon dating (2) Deuterium dating	(1) Nuclear fission (2) Nuclear fusion
(3) Radium dating (4) Uranium dating	(3) Nuclear explosion (4) Chemical reaction
167. Which of the following nuclear reaction occurs in nature	178. Which of the radioactive isotopes is used for temperature
for the formation of tritium?	control in blood disease:
(1) $_{3}\text{Li}^{6} + _{0}n^{1} \longrightarrow _{2}\text{He}^{4} + _{1}\text{H}^{3}$	(1) P^{32} (2) H^3 (3) Rn^{233} (4) I^{131}
$(2) {}_{5}B^{10} + {}_{0}n^{1} \longrightarrow 2 {}_{2}He^{4} + {}_{1}H^{3}$	179. Which of the following is not a fissionable material?
$(3)_{7}N^{14} + {}_{0}n^{1} \longrightarrow {}_{6}C^{12} + {}_{1}H^{3}$	(1) U^{238} (2) U^{233} (3) Pu^{239} (4) U^{235}
$(4)_{4}Be^{9} + {}_{1}D^{2} \longrightarrow 2_{2}He^{4} + {}_{1}H^{3}$	180. A cyclotron is used to
168. The chemist who helped in the discovery of the maximum	(1) Accelerate neutrons (2) Accelerate electrons
number of transuranic element is:	(3) Accelerate protons (4) Accelerate α-particles
(1) Sir Robert Robinson (2) Sir J.J. Thomos	181. In nuclear reactors heavy water is used as a
(3) Professor Sea Borg (4) Sir N.C. Hishelwood	(1) Fuel (2) Projectile (3) Moderator (4) Arrester
169. Artificial radioactivity was first discovered by	182. Slow neutrons can bring about the fission of
(1) Sea Borg (2) Rutherford	$(1)_{92}U^{235}$ $(2)_{82}U^{238}$ $(3)_{82}Pb^{207}$ $(4)_{88}U^{226}$
(3) Einstein (4) Irene Curie	183. Living things contain C^{12} and C^{13} , C^{12} is stable and C^{13}
170. What is X in the nuclear reaction?	decays and declines in proportional quantity. The technique
$_{7}N^{14} + _{1}H^{1} \longrightarrow _{8}O^{15} + X$	that used this principle for determining the age of fossils
$(1)_{1}H^{2}$ $(2)_{0}n^{1}$ $(3)\gamma$ $(4)_{-1}e^{0}$	skeletons, old trees, and dinosaurs is called
171. The reaction	(1) C-12 dating (2) Radiocarbon dating
$_{1}D^{2} + _{1}T^{3} \longrightarrow _{1}He^{2} + _{0}n^{1}$	(3) Carbon age (4) Fossil carbon
is an example of	184. The nuclear process that takes place when a hydrogen bomb
(1) Nuclear fission	is exploded is of the same nature as the process (1) In the centre of the earth
(2) Nuclear fusion	
(3) Artificial radioactivity	(2) In the sun and stars
(4) Radioactive disintegration	(3) During a red dust storm
172. The equipment used to carry out nuclear reaction in a	(4) During atom bomb fission
controlled manner is called	185. Tritium, ₁ H ³ has a half-life of 12.26 yr. A 5.00 mL sample
(1) Breeder reactor (2) Nuclear reactor	of tritiated water has an activity of 2.40×10^9 cpm.
(3) Thermonuclear fission (4) Cyclotron	How many years will it take for the activity to fall to 3.00×10^8 cpm?
173. Which of the following is used as neutron absorber in the	(1) 6.12
nuclear reactor?	(3) 24 52
(1) Water	(4) 30.76
(2) Deuterium	186. In uranium mineral, the atomic ratio $N_{U^{238}}/N_{Pb^{206}}$ is nearly equal to one. The age (in years) of the mineral is
(3) Some compound of uranium	nearly (half-life period of U-238 is 4.5×10^9 yr)
(4) Cadmium	(1) 4.5×10^8 (2) 4.5×10^9
174. The age of rocks on earth or the samples of rocks and dust	$(3) 3.0 \times 10^9 $ $(4) 3.0 \times 10^8$
brought back from the moon can be found by determining	187. There are $0.618 \mu g$ of Ph ²⁰⁶ and $0.228 \mu g$ of $228 \mu g$ or $228 \mu g$
the proportion of radioactive in the rock of dust.	If $T_{1/2}$ of U ²³⁸ is 1.5×10^9 year, age of the rock is
	y, age of the fock is

(1) 0.75 × 10⁹ yr

 $(2) 3.0 \times 10^9 \text{ yr}$

(3) $4.5 \times 10^9 \text{ yr}$

(4) $1.5 \times 10^9 \text{ yr}$

One of the hazards of nulear explosion is the generation of one of the generation of Synamics and its subsequent incorporation in bones. This nuclide St^o and shalf-life of 28.1 years. Suppose one microgram was has a new-born child, how much Sr⁹⁰ will retain in his bones after 20 years?

_{(1) 0.7321} μg

 $(2) 0.6107 \mu g$

(3) 0.5814 μg

(4) $0.2142 \mu g$

Apiece of wood from an archaeological source shows a C¹⁴ activity which is 60% of the activity found in fresh wood today. The age of archaeological sample will be:

(1) 4246 yrs

(2) 4628 yrs

(3) 6248 yrs

(4) 4624 yrs

190. In the nuclear reaction $_{92}U^{232} \rightarrow _{90}Th^{228} +_{2}He^{4}$, (Given: m(U)= 232.038u, m(Th) = 228.0.29u and m(He) = 4.003 u), the ratio of speed of α-particle and speed of light is about

(1) 0.25

(2) 0.036

(3) 0.005

(4) 0.018

191. Which of the following is a spallation reaction?

 $(1)_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} + \gamma$

(2) $_{29}\text{Cu}^{63} + _{2}\text{He}^4 \rightarrow _{17}\text{Cl}^{37} + 16_0n^1 + 14_1\text{H}^1$

 $(3) H^2 + H^2 \rightarrow He^4 + \gamma$

 $(4)_{8}O^{16} + {}_{1}H^{2} \rightarrow {}_{7}N^{14} + {}_{2}He^{4}$

192. A 0.50 g sample of rock was found to have 2.5×10^{-6} mol of $_{19}$ K⁴⁰ ($t_{1/2} = 1.3 \times 10^9$ yr) and 7.5×10^{-6} mol of $_{20}$ Ca⁴⁰. How old is the rock?

(1) $6.5 \times 10^8 \text{ yr}$

(2) $1.3 \times 10^9 \text{ yr}$

 $(3) 2.6 \times 10^9 \text{ yr}$

(4) $5.2 \times 10^9 \text{ yr}$

193. In a sample of wood, the reading of a counter is 32 dpm and in a fresh sample of tree it is 122 dpm. Due to error counter gives the reading 2 dpm in absence of C14. Half life of C14 is 5770 years.

The approximate age (in years) of wood sample is:

(1)7997.2

(2) 57570

(3) 11540

(4) 15140

194. An analysis of the rock shows that the relative number of Sr⁸⁷ and Rb⁸⁷ ($t_{1/2} = 4.7 \times 10^{10}$ year) atoms is 0.05. What is the age of the rock? Assume all the Sr⁸⁷ have been formed from Rb87 only.

(1) 7.62×10^9 years

(2) 1.43×10^9 years

(4) 4.32×10^8 years

195. A radioactive substance (parent) decays to its daughter element. The age of radioactive subtsance (t) is related to the daughter (d)/parent (p) ratio by the equation:

(1) $t = \frac{1}{\lambda} \ln \left(1 + \frac{p}{d} \right)$ (2) $t = \frac{1}{\lambda} \ln \left(1 + \frac{d}{p} \right)$

(3) $t = \frac{1}{\lambda} \ln \left(\frac{d}{p} \right)$

 $(4) t = \frac{1}{\lambda} \ln \left(\frac{p}{d} \right)$

196. The isotopes U^{238} and U^{235} occur in nature in the mass ratio 140:1. It is assumed that initially they were found in equal mass. If half life $(t_{1/2})$ of $U^{238} = 4.5 \times 10^9$ and $t_{1/2}$ of $U^{235} =$ 5×10^8 year respectively, then the age of earth in years is $(\log 7 = 0.846; \log 2 = 0.3)$

 $(1) 4.02 \times 10^9$

 $(2) 2.01 \times 10^9$

 $(3) 8.72 \times 10^9$

(4) None of these

197. Find the age of an ancient Egyptian wooden article (in years) from the given information.

i. Activity of 1 g of carbon obtained from ancient wooden article = 7.7 counts/min/g

ii. Activity of 1 g carbon obtained from fresh wooden sample = 15.4 counts per min/g

iii. Percentage increase in level of C14 due to nuclear explosions in past 100 years is 10%

iv. $t_{1/2}$ of ${}_{6}C^{14} = 5770$ years

 $(1) 5.770 \times 10^3$

(2) 16.87×10^3

(3)2488

(4) None of these

198. Effective neutron capture radius of a nucleus having crosssection of 1.0 barn is:

$$(1) \left(\frac{10^{-28} \, \text{m}^2}{\pi} \right)^{\frac{1}{2}}$$

$$(1) \left(\frac{10^{-28} \,\mathrm{m}^2}{\pi} \right)^{\frac{1}{2}} \qquad (2) \left(\frac{10^{-27} \,\mathrm{m}^2}{\pi} \right)^{\frac{1}{2}}$$

$$(3) \left(\frac{10^{-26} \,\mathrm{m}^2}{2\pi} \right)^{\frac{1}{2}}$$

$$(4) \left(\frac{2\pi}{10^{-27} \,\mathrm{m}^2} \right)^{\frac{1}{2}}$$

199. A radioactive nuclide is produced at a constant rate of α per second. Its decay constant is λ . If N_0 be the number of nuclei at time t = 0, then what will be the maximum number of possible nuclei?

(1) $\frac{\alpha}{\lambda}$ (2) $N_0 + \frac{\alpha}{\lambda}$ (3) N_0 (4) $\frac{\lambda}{\alpha} + N_0$

200. Half life of a radioactive substance A is two times the half life of another radioactive substance B. Initially, the number of nuclei of A and B are $N_{\rm A}$ and $N_{\rm B}$ respectively. After three half lives of A, number of nuclei of both become equal. The ratio of N_A/N_B will be

(1) 1/2

(2) 1/8

(3) 1/3

(4) 1/6

201. The average life of a W g sample of RaE²⁰⁰ is T seconds and the average energy of β -particles emitted is E MeV. At what rate in watts does the sample emit energy?

$$(1) \ \frac{8WN_0E}{T} \times 10^{-1}$$

(1) $\frac{8WN_0E}{T} \times 10^{-16}$ (2) $\frac{8(\ln 2)WN_0E}{T} \times 10^{-13}$

(3) $\frac{8WN_0E}{T} \times 10^{-13}$

(4) None is correct

202. A light nuclide that has n/p ratio 2 and has magic number of neutrons but still shows radioactivity

 $(1)_{2}He^{4}$

 $(2)_{1}H^{3}$

 $(3), H^2$

 $(4)_{2}$ He³

Multiple Correct Answers Type

Radioactivity and Group Displacement Law

- 1. Which of the following statements about radioactivity are correct?
 - (1) It is a nuclear property.
 - (2) It does not involve any rearrangement of electrons.
 - (3) It is not affected by the presence of other elements.
 - (4) Its rate is affected by the change in temperature and/or
- 2. Which among the following nuclides is/are likely to be stable?
 - ${\rm (1)}_{\,49}{\rm In^{114}} \quad {\rm (2)}_{\,12}{\rm Mg^{24}} \quad {\rm (3)}_{\,48}{\rm Cd^{114}} \quad {\rm (4)}_{\,15}{\rm P^{30}}$

- 3. Which of the following nuclei are doubly magic?
 - $(1)_{02}U^{238}$
- $(2)_{2}He^{4}$
- $(3)_{\rm g}O^{16}$
- $(4)_{82} Pb^{208}$
- 4. Which of the following is/are correct?
 - (1) 1 Fermi = $10^3 dps$
- (2) 1 curie = 3.7×10^{10} dps
- (3) 1 rutherford = 10^6 dps (4) 1 becquerel = 1 dps
- 5. Which of the following is/are correct?
 - (1) α -rays are more penetrating than β -rays.
 - (2) α -rays have greater ionizing power than β -rays.
 - (3) β-particles are not present in the nucleus, yet they are emitted from the nucleus.
 - (4) α -rays are not emitted simultaneously with α and β-rays.
- **6.** For emission of α -particle from uranium nucleus:

$$_{92}U^{235} - _{2}He^{4} \longrightarrow _{90}Th^{231}$$

Shortage of two electrons in thorium is due to

- (1) Conversion of electron to positron
- (2) Adsorption in the nucleus
- (3) Annihilation
- (4) Combination with positron to evolve energy
- 7. Radioactivity is generally not found in
 - (1) Light nuclei
- (2) Stable nuclei
- (3) Heavy nuclei
- (4) Nuclei of intermediate mass
- 8. Which of the following statements about radioactivity is/
 - (1) It involves outer electrons activity.
 - (2) It is not affected by temperature or pressure.
 - (3) It is an exothermic process.
 - (4) The radioactivity of an element is not affected by any other element compounded by it.
- **9.** Which of the following contain(s) material particles?
- (1) α -rays
- (2) β -rays
- $(3) \gamma$ -rays
- (4) Anode rays
- **10.** Which of the following is/are not radioactive element(s)?
 - (1) Sulphur
- (2) Tellurium
- (3) Selenium
- (4) Polonium
- 11. Select the correct statement(s):
 - (1) α-particles are simply helium atoms

(2) γ -rays travel with higher speed as compared to α -particle and have higher ionization power as compared to **β**-particle

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(1)

- (3) Loss of β-particles results in the production of isobars
- (4) B-particles are considered as the best bombarding particles
- 12. ₉₂U²³⁸ (III B) undergoes follows emissions

$$^{92}U^{238} \xrightarrow{-\alpha} A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C$$

Which is/are correct statements?

- (1) C will be of III A (boron family group)
- (2) A will be of III B group
- (3) B will be of II A (alkaline earth metal) group
- (4) A will be of I B group
- 13. Which of following options are incorrect regarding the elimination of α and β particles to form an isodiaphere?
 - (1) $n\alpha$, $n\beta$
- (2) $n\alpha$, $(n+1)\beta$

 $(3) n\alpha$

 $(4) n\beta$

Radioactive Disintegration series, n/p ratio, Binding Energy and Packing Fraction

14. A radioactive element A decays by the sequence and with half-lives given below:

$$A \xrightarrow{\alpha \atop 30 \text{ min}} B \xrightarrow{2\beta \atop 2 \text{ days}} C$$

Which of the following statements about this system are

- (1) The mass number of B is greater than A.
- (2) After two hours, less than 10% of the initial A is left.
- (3) Maximum amount of B present at any time is less than 50% of the initial amount of A.
- (4) The atomic numbers of A and C are the same.
- 15. Which of the followings are α -emitters?
 - $(1) Po^{213}$
- $(2) Pb^{215}$
- $(3) Rn^{222}$
- $(4) Ra^{226}$
- 16. Which of the followings nuclides belong to actinium (U^{235}) series?
 - $(1) Pb^{207}$
- $(3) Po^{213}$
- $(4), H^3$

17. In the decay process:

$$A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D$$

 $(2) Po^{215}$

- (1) A and B are isodiaphers (2) A and C are isotones
- (3) A and D are isotopes
- (4) B, C, and D are isobars
- 18. Which of the following is/are incorrect?
 - (1) 1 curie = 3.7×10^{10} dis
 - (2) Actinium series starts with U^{238} .
 - (3) Nuclear isomers contain the same number of protons and neutrons.
 - (4) The decay constant is independent of the amount of the substance taken.
- 19. When nucleus of an electrically neutral atom undergoes a radioactive decay process, it will remain neutral after the decay if the process is:
 - (1) An α-decay
- (2) A y-decay
- (3) A K-capture process
- (4) A β-decay

The correct starting material and product of different starting material and product of different starting material and product of different disintegration series is/are

(1) Th²³², Pb²⁰⁸

(2) Np^{237} , Bi^{209}

(4) U^{238} , Pb^{206}

(3) U²³⁵, Pb²⁰⁶ Which of the following is/are correct when a nuclide of mass 0 which of the following is/are correct when a nuclide of mass 0 where 0 and atomic number 0 under 0Which is a number (A) and atomic number (Z) undergoes radioactive number (Z)

- Both A and Z decrease, the process is called α -decay.
- (1) A remains unchanged and Z decreases by 1. The process is called β^{\oplus} or positron decay or K-electron capture.
- $_{(3)}$ Both A and Z remain unchanged, the process is called
- $_{(4)}$ Both A and Z increase, the process is called nuclear isomerism.
- 12. The nuclide X undergoes α -decay and another nuclides Y undergoes β[©]-decay, which of the following statements is/ are correct?
 - (1) The β^{\odot} -particles emitted by Y may have widely different
 - (2) The α -particles emitted by X may have widely different
 - (3) The α -particles emitted by X will have almost same speed.
 - (4) The β -particles emitted by Y will have the same speed.
- 23. The mass defect of the nuclear reaction $_5B^8 \longrightarrow {}_4Be^8 + {}_1e^0$ is Δm ; the wrong expression is/are
 - (1) Δm = atomic mass of ($_4$ Be⁸ $_5$ B⁸)
 - (2) Δm = atomic mass of ($_4$ Be⁸ $_5$ B⁸) + mass of one electron
 - (3) $\Delta m = \text{atomic mass of } (_4\text{Be}^8 _5\text{B}^8) + \text{mass of one positron}$
 - (4) $\Delta m = \text{atomic mass of } (_4\text{Be}^8 _5\text{B}^8) + \text{mass of two electrons}$
- 24. Which of the following elements have binding energy per nucleon less than 7?

 $(1)_{3}Li^{6}$

 $(2)_{26} Fe^{56}$

 $(3)_5 B^{10}$

 $(4)_{6}C^{12}$

25. Mass of 1 amu gives energy equal to

(1) 9×10^6 ergs

(2) 931.5 MeV

(3) $1.494 \times 10^{-10} \text{ J}$

(4) $9 \times 10^{13} \text{ J}$

- 26. In electron capture (radioactive process):
 - (1) A neutron is formed
 - (2) A proton is consumed
 - (3) γ-ray emission takes place
- 27. Select the correct statement(s) for positron emission by unstable nucleus.
 - (1) X-ray emission takes place
 - (2) A neutron is formed
 - (3) $\frac{n}{p}$ of daughter nucleus increases
 - (4) A neutron is consumed

- **28.** Select the correct statement(s):
 - (1) Mass number remains constant when positron emission takes place
 - (2) One neutron converts into proton in β ($_1e^0$) emission process
 - (3) Activity of a radioactive substance double when temperature increases from 300 K to 310 K
 - (4) Isodiaphers formed when one alpha particle emited and isotopes formed when 2 beta particles emitted

Rate of Disintegration, Half and Average Life

- 29. The half life period of a radioactive element does not depend upon:
 - (1) Temperature
 - (2) Pressure
 - (3) Initial amount of radioactive element taken
 - (4) Nature of radioactive element
- 30. Radon undergoes decay by α -emission

$$_{88}\text{Rn}^{222} \xrightarrow{t_{1/2} = 3.8 \text{ decay}} _{84}\text{Po}^{218} + _{2}\text{He}^{4}$$

Which of the following statements will be true of this decay

- (4) If the initial amount of radon was 1 mg, the amount of radon left after 11.4 days will be 0.125 mg.
- (2) Activity of radon after 7.6 days will be $N_0 \times (5.3 \times 10^{-7}) \,\text{s}^{-1}$ where N_0 is the original number of atoms of the radon.
- (3) The decay constant of radon is $2.1 \times 10^{-6} \text{ s}^{-1}$
- (4) 60% of the radon will decay in 5 days approximately
- 31. It is observed that only 0.39% of the original radioactive sample remains undecayed after eight hours. Hence:
 - (1) The half-life of that substance is 1 hour
 - (2) The mean life of the substance is $\frac{1}{\log_2 2}$ hour
 - (3) Decay constant of the substance is $(\log_e 2)$ hour⁻¹
 - (4) If the number of radioactive nuclei of this substance at a given instant is 108, then the number left after 30 min would be $\sqrt{2} \times 10^9$
- 32. A counter rate meter is used to measure the activity of a radioactive sample. If at certain instant, the count rate was recorded as 475 counter per minute. Five minutes later, the count rate recorded was 270 couts per minute. What is the half life period of the sample in minutes?

(1) 3.0

(2) 3.5

(3) 5.0

(4) 6.0

Artificial Tansmutation, Nuclear Reaction and Applications of Radioactivity

- 33. In a nuclear reactor, heavy water is used to
 - (1) Increases the speed of neutrons
 - (2) Decreases the speed of neutrons (3) Transfer the heat from the reactor
 - (4) None of above

6.60	Physical	Chemistr

- 34. Which among the following is/are fissible?
 - $(1)_{92}U^{235}$
- $(2)_{92}U^{238}$
- $(4)_{94} Pu^{238}$
- $(3)_{94} Pu^{239}$ 35. Which of the following is/are true?
 - (1) The most radioactive element present in pitchblende is uranium.
 - (2) P-32 is used for the treatment of leukaemia.
 - (3) CO₂ present in the air contains C-12 only.
 - (4) Omission of γ-rays changes the mass number but not atomic number.
- 36. Which of the following is/are the examples of induced radioactivity?
 - $(1)_{7}N^{14} + _{7}He^{4} \longrightarrow _{8}O^{17} + _{1}H^{1}$
 - (2) $_{4}\text{Be}^{9} + _{1}\text{H}^{1} \longrightarrow {}_{3}\text{Li}^{9} + _{2}\text{He}^{4}$
 - (3) $_{12}Mg^{24} + _{2}He^4 \longrightarrow {}_{14}Si^{27} + _{0}n^1$
 - $(4) {}_{5}B^{10} + {}_{2}He^{4} \longrightarrow {}_{7}N^{13} + {}_{0}n^{1}$
- 37. Which one of the following statements is/are correct?
 - (1) Neutron was discovered by Chadwick.
 - (2) Nuclear fission was discovered by Hahn and Strassmann.
 - (3) Polonium was discovered by Madam Curie.
 - (4) Nuclear fusion was discovered by Fermi.
- 38. Select the correct statements:
 - (1) In the nuclear process:

$$_{96}U^{241} + _{2}He^{4} \longrightarrow _{97}Bk^{244} + _{+1}e^{0} + X$$

X stands for neutron

(2) In the nuclear process:

$$_{6}C^{11} \longrightarrow _{5}B^{11} + \beta^{\oplus} + X$$

X stands for neutrino

(3) In the nuclear process:

$$_{1}H^{3} \longrightarrow _{2}He^{3} + _{-1}e^{0} + X$$

X stands for antineutrino.

- (4) The rest mass of a stable nucleus is lesser than the sum of rest masses of its separated nucleons.
- **39.** Select the correct statements:
 - (1) In nuclear reactor, cadmium is used to absorb neutrons.
 - (2) In nuclear reactor, molten sodium is used for transferring heat generated from the reactor to a turbine steam boiler i.e., acts as a heat exchanger.
 - (3) Carbon-14 dating method is based on the fact that ratio of C-14 and C-12 remains constant during disintegration.
 - (4) As⁷⁴ is used to locate blood clots and circulatory disorder
- **40.** Select the correct statement(s):
 - (1) In the reaction $_{92}U^{235} + _{0}n^{1} \longrightarrow _{56}Ba^{140} + 2_{0}n^{1} + x, x$
 - (2) In the reaction ${}_{11}\text{Na}^{23} + z \longrightarrow {}_{12}\text{Mg}^{23} + {}_{0}n^{1}$, the bombarding particle z is deuteron
 - (3) Very large amount of energy is produced during nuclear fisson and nuclear fussion
 - (4) In a fission reaction, a loss in mass occurs releasing a vast amount of enegy

- 41. Assuming that about 200 MeV of energy is released per fission of 92U²³⁵ nuclei, then the mass of U²³⁵ consumed per day in a fission reactor of power 1 megawatt will be approximately:
 - $(1)\ 10^{-2}\ g$
- (2) 1 g

- (3) 100 g
- (4) 1000 g

Linked Comprehension Type

Paragraph 1

The activity of a nucleus is inversely proportional to its half or average life. Thus, shorter the half life of an element, greater is its radioactivity, i.e., greater the number of atoms disintegrating per second. The relation between half life and average life is

$$t_{1/2} = \frac{0.693}{\lambda} = \tau \times 0.693$$

or $\tau = 1.44t_{1/2}$

- 1. The half life of a radioactive element is 10 years. What percentage of it will decay in 100 years?
 - (1) 99.9%
- (2) 10%
- (3)50%
- (4) 66.5%
- 2. The half-life periods of four isotopes are given I = 6.7 years: II = 8000 years; III = 5760 years; IV = 2.35×10^5 years. Which of these is most stable?
 - (1)I
- (2) II
- $(3) \coprod$
- (4) IV
- 3. Mark the incorrect relation.

$$(1) N_0 = Ne^{\lambda t}$$

(2)
$$\tau = 1.44t_{0.5}$$

$$(3) N = N_0 \left(\frac{1}{2}\right)^n$$

(4)
$$t_{1/2} = 2.303\lambda \log 2$$

Paragraph 2

Unstable nuclei attain stability through disintegration. The nuclear stability is related to neutron proton ratio (n/p). For stable nuclei n/p ratio lies close to unity for elements with low atomic numbers (20 or less) but it is more than 1 for nuclei having higher atomic numbers. Nuclei having n/p ratio either very high or low undergo nuclear transformation. When n/p ratio is higher than required for stability, the nuclei have the tendency to emit β -rays. While when n/p ratio is lower than required for stability, the nuclei either emits α -particles or a positron or capture K-electron.

- 4. Unstable substance exhibit high radioactivity due to
 - (1) Low p/n ratio
- (2) high p/n ratio
- (3) p/n = 1
- (4) None
- 5. β -particle is emitted in radioactivity by
 - (1) Conversion of proton to neutron
 - (2) Conversion of neutron to proton
 - (3) β-particle is not emitted
 - (4) None
- 6. For reaction $_{92}M^{238} \longrightarrow _{\nu}N^{x} + 2_{2}He^{4}; _{\nu}N^{x} \longrightarrow _{B}L^{A}$ $+2_{-1}e^{0}$

The number of neutrons in the element L is

- (1) 140
- (2) 145
- (3) 138
- (4) 160

1. Among the following nuclides, the highest tendency to decay by β[®] emission is

- (1) Cu⁶⁸
- $(2) Cu^{59}$
- (3) Cu⁶⁸
- $(4) Cu^{67}$

- $^{(3)}_{\text{8.13}}$ Al²⁷ is a stable isotope; $_{13}$ Al²⁹ is expected to disintegrate
- (1) β -emission
- (2) α -emission
- (3) y-emission
- (4) Positron emission

_{paragraph} 3

prigration of a radioactive element, α - and β -particles the nucleus ne evolved from the nucleus.

$$e^{\text{volved}}$$
 from the nucleus.
 e^{volved} from the nucleus.

Then, emission of these particles changes the nuclear configuration α and α daughter nuclide. Emission of an α -particle and a daughter element having atomic number lowered by 2 and mass number by 4; on the other hand, emission of a β -particle yelds an element having atomic number raised by 1.

- 9. Which of the following combinations give finally an isotope of the parent element?
 - $(1) \alpha, \alpha, \beta$
- $(2) \alpha, \gamma, \alpha$
- $(3) \alpha, \beta, \beta$
- $(4) \beta, \gamma, \alpha$
- 10. A radioactive element belongs to III B group; it emits one αand one β -particle to form a daughter nuclide. The position of daughter nuclide will be in
 - $(1) \coprod A$

(2)IA

(3) II B

- (4) IVB
- 11. During β -decay, the mass of atomic nucleus
 - (1) Decreases by 1 unit
- (2) Increases by 1 unit
- (3) Decreases by 2 units
- (4) Remains unaffected
- 12. How many α and β -particles should be emitted from a radioactive nuclide so that an isobar is formed?
 - $(1)1\alpha$, 1β
- $(2) 1\alpha, 2\beta$
- $(3) 2\alpha, 2\beta$
- (4) $n\beta$
- 13. Select the correct statements among the following:
 - (1) Emission of a β -particle results into an isobar of parent
 - (2) Emission of α -particle results into an isodiapher of
 - (3) Emission of one α and two β -particles results into an isotope of the parent element.
 - (4) Emission of γ -radiations may yield a nuclear isomer.

Paragraph 4

Uranium ($_{92}U^{238}$) decayed to $_{82}Pb^{206}$. The decay process is

$$_{92}U^{238} \xrightarrow{(x\alpha,y\beta)} {}_{82}Pb^{206}$$

 $t_{1/2}$ of $U^{238} = 4.5 \times 10^9$ years

- 14. x and y in above decay series are
 - (1)6,8

- (2)9,6
- (3) 8, 8
- (4) 8, 6

- 15. A sample of rock from South America contains equal number of atoms of U²³⁸ and Pb²⁰⁶. The age of the rock will be
 - (1) 4.5×10^9 years
- (2) 9×10^9 years
- (3) 13.5×10^9 years
- (4) 2.25×10^9 years
- 16. Atomic mass of U²³⁸ is 238.125 amu. Its packing fraction will be
 - (1) 6.25
- (2) 0.125
- (3) 12.5
- (4) 5.25
- 17. The analysis of a rock shows the relative number of U^{238} and Pb^{206} atoms (Pb/U = 0.25). The age of rock will be
 - (1) $\frac{2.303}{0.693} \times 4.5 \times 10^9 \log 1.25$
 - (2) $\frac{2.303}{0.693} \times 4.5 \times 10^9 \log 0.25$
 - (3) $\frac{2.303}{0.693} \times 4.5 \times 10^9 \log 4$
 - (4) $\frac{2.303}{4.5 \times 10^9} \times 0.693 \log 4$

Matrix Match Type



This section contains questions each with two columns—I and II. Match the items in column I with that in column II.

	Column I		Column II
a.	2/3rd life	p.	63.2% decay
b.	Average life	q.	75% decay
	1/λ	r.	$2 \times t_{1/2}$
d.	Ten times of half life	s.	99.9% decay
e.	X-rays	t.	Radiations undeviated in electric field

•	Column I		Column II
a.	4n	p.	Uranium series
b.	4n + 1	q.	Neptunium series
c.	4n + 2	r.	Actinium series
d.	4n + 3	s.	Thorium series

3.		Column I		Column II
	a.	$_{4}\text{Be}^{9} + _{2}\text{He}^{4} \rightarrow _{6}\text{C}^{12} + \dots$	p.	₂ He ⁴
	b.	$_{6}$ C ¹² + \rightarrow $_{5}$ B ¹⁰ + $_{2}$ He ⁴	q.	$_{0}^{n^{1}}$
	c.	$_{7}N^{14} + \rightarrow _{8}O^{17} + _{1}H^{1}$	r.	$_{l}D^{2}$
	d.	$_{20}$ Ca ⁴⁰ + $\rightarrow _{19}$ K ³⁷ + $_{2}$ He ⁴	s.	lH1
	e.	$_{83}\text{Bi}^{209} + _{2}\text{He}^{4} \rightarrow _{85}\text{At}^{211} + \dots$	t.	1123

	Column I		Column II
	Series	MAN IN	Particles emitted
a.	Thorium	p.	8α, 5β
b,	Neptunium	q.	8α, 6β
c.	Actinium	r.	6α, 4β
d.	Uranium	s.	7α, 4β

	Column I (Isotope)		Column II (Characteristics)
a.	₂₀ Ca ⁴⁰	p.	Unstable, positron emitter
b.	₅₃ I ¹³³	q.	Unstable, β-emitter
c.	₅₃ I ¹²¹	r.	Unstable, α-emitter
d.	₉₀ Th ²³²	s.	Stable
e.	₆ C ¹⁴		
f.	$_{7}N^{13}$		

6.		Column I (Particles emitted)		Column II (Result)
	a.	One α-particle	p.	Isobar
	b.	One α- and two β-particles	q.	Isotope

c.	One β-particle	r.	Isodiapher
d.	γ-radiation	s.	Atomic number reduce by two and mass numbe by four
		t.	Nuclear de-excitation

	Column I		Column II
a.	Probability of survival of a radioactive nucleus for one mean life	p.	N ₀ (2)-"
b.	Amount remaining after <i>n</i> half lives	q.	$e^{\lambda(t1-t0)}$
c.	$\frac{R_2}{R_1}; R_1 = \text{Rate at time } t_1$ $R_2 = \text{Rate at time } t_2$	r.	$\left(\frac{1}{2}\right)^{11/10}$
d.	Amount left on 11th day, starting with 1 mol of A $(t_{1/2} = 10 \text{ days})$	s.	1/ <i>e</i>

For Q.8 to Q.11

Answer the question given below by appropriately matching the information given in three column of the following table

	Column I		Column II		Column III
	n/p ratio		n/p ratio of daughter element		Process
a	Nuclides with atomic number less than 82 and with very low n/p ratio	i	$\left(\frac{n-2}{z-2}\right)$	p	$p \rightarrow n + \beta^{\oplus}$
b	Nuclides with atomic number less than 82 with very high n/p ratio	ii	$\left(\frac{n+1}{z+1}\right)$	q	α-emissiom
c	Nuclides with atomic number greater than 82 and n/p ratio becomes stable	iii	$\left(\frac{n-1}{z+1}\right)$	r	$n \to p + \beta^{\Theta}$
		iv	Stability is due to $n-p$ and $p-p$ attractive forces operating at nuclear distance.	s	k-capture
	1. 2. 1830 - V.	v	Stability is due to reduction of $p-p$ repulsion and excess of neutrons over protons.		

- **8.** For the nuclides ($_{80}$ Hg 195 and $_{67}$ H $_{\rm O}$ ¹⁵⁰), the only correct combination is:
 - (1) a—ii, iv—p
- (2) b—iii, iv—r
- (3) c—i, v—q
- (4) a—ii, iv—s
- 9. For the nuclides. ($_{13}A1^{30}$ and $_{36}Kr^{94}$), The onlt correct combination is:
 - (1) a—ii, iv—p
- (2) b—iii, iv—r
- (3) c-i, v-q
- (4) a—ii, iv—s
- 10. Which of the following processes cause in decrease in atomic number?

- (2) p, q, r(3) q, r, s (4) q, s (1) p, q, s 11. Which of the following processes cause emission of X-ray
- (1) p, q
- (2) q, r
- (3) Only r
- (4) Only s

Numerical Value Type



- 1. An emission of α particle decreases the atomic number of parent element by
 - (1)4
- (2)2
- (3) 3
- (4) 1
- 2. An emission of β particle increases the atomic number of parent element by
 - (1) 1
- (2) 2
- (3) 3
- (4)4
- 3. How many α particles will be emitted when $_{90}\text{Th}^{234}$ changes into ₈₄Po²¹⁸?
 - (1) 1
- (2) 2
- (3) 3
- (4)4
- 4. After 20 min, the amount of certain radioactive substance disintegrate was 15/16th of the original amount. What is the half-life of the radioactive substance?
 - (1)4
- (2) 6
- (3)5
- (4) 8

The half-life period of a radioactive substance is 2 min. The taken for 1 g of the substance to reduce to 0.27 The hall-life F 1 g of the substance to reduce to 0.25 g will be

(2)4

Numeron Number 1 Num

(2)7

(4)9

Upon the U^{235} nucleus absorbs a neutron and disintegrates into U^{235} nucleus absorbs a neutron and disintegrates into U^{235} nucleus absorbs a neutron and disintegrates into $^{2^{1}}_{x^{0}}$ $^{139}_{x^{0}}$, $^{38}_{38}$ Sr 94 , and x. What will be the product x?

(1) 3 neutrons

(3) 2 α -particles

(4) 2 B-particles

The half life of C-14 is 5600 years. A sample of freshly cut wood from a tree contains 10 mg of C-14. The amount left in the sample after 50000 years is $(a - x) \times 100$. The value $_{\text{of}(a-x)} \times 100 \text{ is}$

(1) 1

(2) 2

(3)3

(4)4

o In the following given numbers, how many are the magic numbers?

2,820,50,113,126,141,148,300,314

(1)4

(2)7

(3)5

(4)9

10. For a nuclear reaction, the mass defect is 0.00859 amu. Calculate the energy released in MeV.

(1)6

(2)9

(4)8

11. If $t_{3/4}$ and $t_{1/2}$ are time required for completion of 3/4 decay and 1/4 decay, then $t_{3/4} = t_{1/2} \times n$. *n* is:

12. A positron and an electron collide and annihilated to emit two gamma photons of same energy. Calculate the wavelengths in pm corresponding to this gamma emission.

13. If one starts with 1 Curie (Ci) of radioactive substance $(t_{1/2} = 15 \text{ hr})$, the activity left after a period of two weeks will be about $0.02 x \mu \text{Ci}$. Find the value of x.

14. If 80% of a radioactive element undergoing decay is left over after a certain period of time t from the start, how many such periods should elapse from the start for just over 50% of the element to be left over?

15. Total number of nuclides which are β^{\oplus} emitter are:

I. 20Ca⁴⁹

II. 80Hg¹⁹⁵

IV. ₆₇Ho¹⁵⁰ V. ₁₃Al³⁰ VI. ₃₆Kr³⁹

Archives

FE ADVANCED

Single Correct Answer Type

1. Bombardment of aluminium of α-particle leads to its artificial disintegration in two ways (i) and (ii) as shown below. Product X, Y, and Z, respectively, are

$$_{14}\text{Si}^{30} + X \xleftarrow{(i)}{_{13}}\text{Al}^{27} \xrightarrow{(ii)}{_{15}} P^{30} + Y \xrightarrow{}_{14}\text{Si}^{30} + Z$$

(1) Proton, neutron, positron (2) Neutron, positron, proton

(3) Proton, positron, neutron (4) Positron, proton, neutron (IIT-JEE 2011)

Multiple Correct Answers Type

1. In the nuclear transmutation

 $_{4}Be^{9} + X \longrightarrow _{4}Be^{8} + Y$ (X,Y) is/are

(1)(y, n)

21.(3)

(2)(p, D)

(3)(n, D)(JEE Advanced 2013)

 $(4)(\gamma, p)$

2. A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upwards deviation from linearity for atomic number, Z > 20. For an unstable nucleus having N/P ratio less than 1, the possible mode(s) of decay is(are).

(1) β^- -decay (β emission)

(2) orbital or K-electrons capture

(3) neutron emission

(4) β^+ -decay (positron emission)

(JEE Advanced 2016)

Numerical Value Type

1. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table?

$$_{29}\text{Cu}^{63} + _{1}\text{H}^{1} \longrightarrow 6_{0}\text{n}^{1} + _{2}\text{He}^{4}(\alpha) + 2_{1}\text{H}^{1} + _{2}\text{X}^{A}$$

(IIT-JEE 2012)

2. A closed vessel with rigid walls contains 1 mol of $\frac{238}{92}$ U and 1 mol of air at 298 K. Considering complete decay of $^{238}_{92}$ U to $^{206}_{82}$ Pb, the ratio of the final pressure to the initial pressure of the system at 298 K is (JEE Advanced 2015) **EXERCISES**

Answers Key

Single Correct Answer Type

22. (4)

5.(1) 4. (4) 3. (1,3,4) 1.(2)**2.**(1) 9. (1) 8. (3) 7.(4)14. (4) 6.(3)13. (4) 19. (4) 11.(1)**12.** (4) 18. (2) **17.**(1) 24. (2) 16.(3)23. (4)

10.(3) 15.(2) 20. (2) **25.** (2) 26.(2) 27. (4) **28.** (1) **29.** (2) 31.(2) **30.** (2) **32.**(1) **33.** (1) 34. (2) 36.(2) 35.(2) 37.(1) **38.** (1) 39. (3) 41.(4) **40.** (3) **42.**(2) 43. (2) 44. (2) 46.(2) 45.(2) 47. (4) 48. (4) 51.(2) 49. (3) **50.** (4) 52.(2) 53. (4) 54. (4) **55.** (1)

			and the second of the second o	
54. (1)	57. (2)	58. (1)	59. (2)	60. (3)
01.(1)	62. (4)	63. (2)	64. (1)	65. (4)
00. (3)	67. (3)	68. (1)	69. (3)	70. (1)
71.(4)	72. (1)	73. (1)	74. (1)	75. (2)
76. (4)	77. (4)	78. (1)	79. (1)	80. (2)
81.(3)	82. (4)	83. (3)	84. (3)	85. (3)
86. (2)	87. (3)	88. (2)	89. (3)	90. (3)
91.(2)	92. (3)	93. (3)	94. (2)	95. (2)
96. (2)	97. (3)	98. (1)	99. (2)	100. (2)
101. (1)	102. (3)	103. (2)	104. (4)	105. (1)
106. (1)	107. (1)	108. (1)	109. (4)	110. (1)
111. (2)	112. (1)	113. (4)	114. (3)	115. (4)
116. (4)	117. (1)	118. (1)	119. (3)	120. (1)
121. (3)	122. (2)	123. (3)	124. (2)	125. (1)
126. (2)	127. (4)	128. (2)	129. (2)	130. (3)
131. (2)	132. (1)	133. (2)	134. (2)	135. (4)
136. (3)	137. (2)	138. (2)	139. (3)	140. (1)
141. (3)	142. (3)	143. (4)	144. (2)	145. (4)
146. (3)	147. (2)	148. (3)	149. (2)	150. (1)
151. (3)	152. (2)	153. (3)	154. (3)	155. (4)
156. (3)	157. (2)	158. (2)	159. (3)	160. (1)
161. (4)	162. (3)	163. (3)	164. (2)	165. (2)
166. (1)	167. (3)	168. (3)	169. (4)	170. (3)
171. (2)	172. (2)	173. (4)	174. (2)	175. (3)
176. (1)	177. (2)	178. (1)	179. (1)	180. (3)
181. (3)	182. (1)	183. (2)	184. (2)	185. (4)
186. (2)	187. (2)	188. (2)	189. (1)	190. (3)
191. (2)	192. (3)	193. (3)	194. (3)	195. (2)
196. (1)	197. (1)	198. (1)	199. (1)	200. (2)
201. (1)	202. (2)			

Multiple Correct Answers Type

1. (1, 2, 3)	2. (2, 3)	3. (2, 3, 4)
4. (3, 4)	5. (2, 3, 4)	6. (3, 4)
7. (1, 2, 4)	8. (2, 3, 4)	9. (1, 2, 4)
10. (1, 2, 3)	11. (1, 3)	12. (2, 3)
13. (1, 2, 4)	14. (2, 4)	15. (1, 4)
16. (1, 2)	17. (1, 3, 4)	18. (3, 4)
19. (2, 3)	20. (1, 4)	21. (1, 2, 3)
22. (2, 3)	23. (1, 2, 3)	24. (1, 3)
25. (2, 3)	26. (1, 2)	27. (2, 3)

20 (1 2)	20 (1 2 2)	30. (1, 2, 3, 4)
28. (1, 2)	29. (1, 2, 3)	30. (1, 2, 3, 4)
31. (1, 2, 3)	32. (4)	33. (2, 3)
34. (1, 3)	35. (2, 3)	36. (1, 2, 3, 4)
37. (1, 2, 3)	38. (1, 2, 3, 4)	39. (1, 2, 3)
40. (1)	41. (2)	

Linked Comprehension Type

1.	(1)	2. (4)	3. (4)	4. (1)	5. (2)
6.	(1)	7. (4)	8. (1)	9. (3)	10. (1)
11.	(4)	12. (4)	13. (1,2,3,	,4)14. (4)	15. (1)
16.	(4)	17. (1)			

Matrix Match Type

Q.No.	a	b	c	d	e	f
1.	q, r	р	р	s	t	_
2.	S	q	р	r	_	_
3.	q	r	р	S	q	_
4.	r	p	S	q	_	
5.	S	q	р	r	q	p
6.	r, s	q	р	t	_	_
7.	s	p	q	q		

			40 (4)	44 (4)
8.	(1)	9. (2)	10. (1)	11. (4)

Numerical Value Type

1. (2)	2. (1)	3. (4)	4. (3)	5. (2)
6. (4)	7. (1)	8. (2)	9. (3)	10. (4)
11. (2)	12. (2)	13. (9)	14. (3)	15. (3)

ARCHIVES

JEE Advanced

Single Correct Answer Type

1. (1)

Multiple Correct Answers Type

1. (1, 2) **2.** (2, 4) **Numerical Value Type**

1. (8)

2. (9)